METALLURGIA

THE BRITISH JOURNAL OF METALS

Vol. 47 No. 279 JANUARY, 1953 Monthly: TWO SHILLINGS

19 JAN 1953

Saving fuel

KENT R·S·C

meter for small process steam mains, and for feed

SAVING FUEL

This interesting folder is available on reques from

GEORGE KEN LIMITED LUTON

RESEARCH
I.E.I.
LABORATORY

METALLURGIA

THE BRITISH JOURNAL OF METALS

INCORPORATING THE METALLURGICAL ENGINEER

CONTENTS FOR JANUARY, 1953 Vol. 47 No. 279

PUBLISHED MONTHLY BY

The Kennedy Press, Ltd.,
31, King Street West,
Manchester, 3.
Telephone : BLAckfriars 2084

London Office :
21, Bedford Street, W.C.2.
Telephone : Temple Bar 2629

CONTRIBUTIONS

Readers are invited to submit articles for publication in the editorial pages: photographs and/or drawings suitable for reproduction are especially welcome. Contributions are paid for at the usual rates. We accept no responsibility in connection with submitted manuscript. All editorial communications should be addressed to The Editor, "Metallurgia," 31, King Street West, Manchester, 3.

SUBSCRIPTIONS

Subscription Rates throughout the World—24/- per annum, Post free.

ADVERTISING

Communications and enquiries should be addressed to the Advertisement Manager at Manchester.

	Page
Room at the Top	1
New Year Honours	2
Developments in Alloy Steels: A Review of Recent Progress. By C. Sykes	3–8
Correspondence: Silver Brazing of Stainless Steel	8
Copper and Copper Alloys: A Survey of Technical Progress during 1952. By E. Voce	9–17
Behaviour of Carbides in Niobium Stabilised Austenitic Stainless Steel. By T. V. Simpkinson	18–24
New and Revised Standards	24
Automatic Control of Open Hearth Furnaces. Comprehensive Installation at Shotton	25–26, 38
An Examination of Joule's Work on the Metallurgy of Amalgams. By H. J. Axon	27–28
A Sterling Silver Containing Aluminium. By G. E. Gardam	29–33
Unorthodox Methods of Machining Hard Materials. By P. Grodzinski	34–38
News and Announcements	39–40
Recent Developments	41
Current Literature	42
Metallurgical Digest	43–44

LABORATORY METHODS SUPPLEMENT

Recent Developments in Metallurgical Analysis. II—Titrimetric Methods. By T. S. West	45–51
Miscellaneous Microchemical Devices. XXVII—A Simple Low-Pressure Hydrogen Sulphide Generator. By J. T. Stock and P. Heath	51
British Standard Analytical Methods for Iron and Steel	52

The articles in this Journal are indexed in THE INDUSTRIAL ARTS INDEX

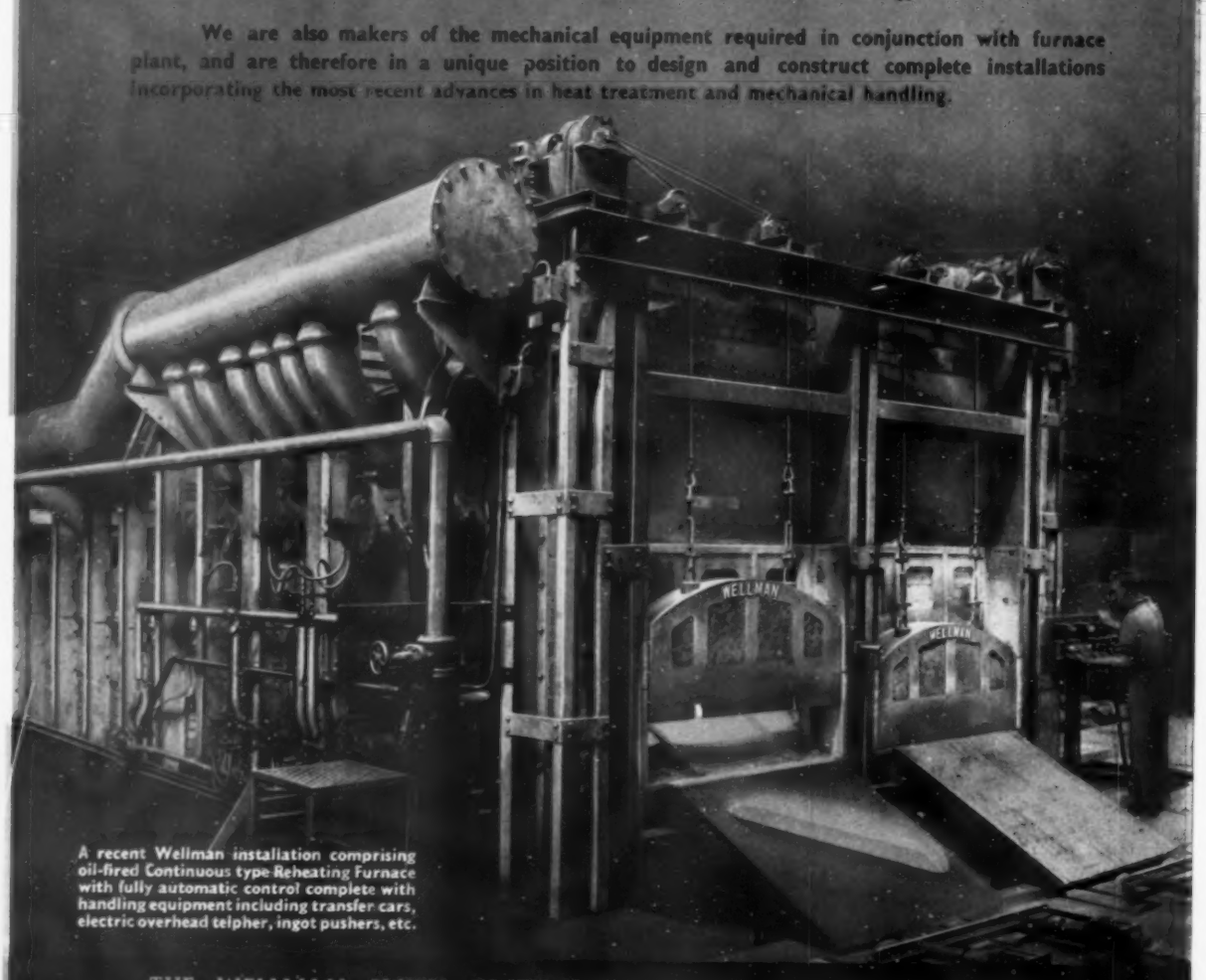
WELLMAN

Re-Heating and Heat Treatment Furnaces for the Metallurgical Industries

We design and construct Re-Heating and Heat Treatment Furnaces of many types for both ferrous and non-ferrous trades ranging from small units dealing with castings of a few pounds each up to the largest Bogie Heat Treatment Furnaces handling single pieces of 100-tons and upwards.

With the increased demands for precision and for constant quality, automatic control of furnace conditions is recognised as essential and this subject has received special attention in our engineering and research departments where every aspect of heating technology is studied.

We are also makers of the mechanical equipment required in conjunction with furnace plant, and are therefore in a unique position to design and construct complete installations incorporating the most recent advances in heat treatment and mechanical handling.



A recent Wellman installation comprising oil-fired Continuous type Reheating Furnace with fully automatic control complete with handling equipment including transfer cars, electric overhead telpher, ingot pushers, etc.

THE WELLMAN SMITH OWEN ENGINEERING CORPORATION LIMITED
PARNELL HOUSE, WILTON ROAD, LONDON, S.W.1. WORKS: DARLASTON, SOUTH STAFFS.

METALLURGIA

THE BRITISH JOURNAL OF METALS

INCORPORATING THE "METALLURGICAL ENGINEER"

JANUARY, 1953 Vol. XLVII. No. 279

Room at the Top

A FIRM belief that management of industry in general has not at present enough engineers and scientists among its ranks was expressed by Mr. H. C. I. Rogers, Chief Engineer and Director of The Imperial Tobacco Co. (of Great Britain and Ireland), Ltd., in the course of a paper read recently before the Western Branch of the Incorporated Plant Engineers, on the grounds that, given a right engineering training, engineers can make a most valuable contribution to the great majority of managerial problems. Although the paper was mainly concerned with engineers, similar arguments could be put forward on behalf of the claims of scientists for consideration in making management appointments. It is a strange fact, as Mr. Rogers pointed out, that whilst those with a scientific training seem to be unable to attain to the greatest heights of management, others trained in professions involving almost equally precise and logical mental processes—the solicitors and the accountants—are much more successful. It is evident, however, that management will not bring engineers and scientists into its ranks unless, on the one hand, the engineers and scientists themselves have ambitions to get there, and unless, on the other, they appear to have the qualities, particularly of character, that will make them valuable recruits to management.

It has been said that the best scientists are those who start off with an intense interest in science. Whilst this is probably true, in general, it is by no means certain that such scientists would make the best managers—in fact, their devotion to science might make them totally unsuited for managerial positions. To one whose interest in science amounted almost to a passion, an exchange leading to divorce from research and development work, and an association with all the mundane business of management, salaries and wages, sales programmes, plant and buildings, maintenance, etc., could seem to be no more than an exchange for a lower and duller set of problems. It is not surprising, therefore, that an appreciable proportion of scientists engaged in industry have not the slightest ambition to enter the management field.

Reference has been made to the appointment of lawyers and accountants to the boards of management of many of the larger concerns, and there are, of course, sound reasons for the adoption of such a policy. Nevertheless, there appear to be equally good reasons why scientists—using the term in its broadest sense—should also be given positions in higher management. It may be argued that where a man has taken an active part in the technical work involved in the development of a new process or a new product, he may be over-enthusiastic in advocating its adoption, and that the analytical study of the economic aspects of the matter by non-technical men is an essential requirement before any far-reaching decision can be made. Such a view is taken by those who regard the scientist as suitable for acting in an advisory capacity, but not capable of making decisions on matters of policy.

The question arises as to whether such a view is correct, and if so, how can the situation be remedied? Undoubtedly, one would not hesitate to admit that there are scientists who would be incapable of making such decisions: on the other hand it would be equally true to say that there are lawyers and accountants in the same category. That is a matter of individual personalities, but, apart from inherent qualities in the individual, the question of education and training arises. No matter what course is taken at the university, whether it be classics, law, medicine, mathematics, science or engineering, the main object is to try to teach the student to think clearly and honestly, and if success in this is achieved, the foundation is laid for building up that prime requisite of management—a sound judgment. If to this is added a thorough knowledge of the fundamentals of science and a scientific approach to day-to-day problems, whether technical or otherwise, there seems no fundamental reason why a scientist should not prove suitable for appointment to a managerial position. Generally speaking, however, there are two reasons why such appointments are not made more often than they are. Many of the best scientists in the country have sound ideas, but are quite unable to give expression to them in a way which would attract the attention of top management—and before one can graduate into top management one has to attract its attention. In the second place, the majority of scientists have never had sufficient grounding—if they have had any at all—in economics. Considerable concern is felt in many quarters about the low standard of self-expression, and whilst the universities have a responsibility in the matter, the foundation should have been laid before entrance.

One essential of a successful leader is the possession of a good imagination, and if the scientist goes on being nothing but a scientist for too long, the imaginative approach so necessary for management seems to disappear. It, follows, therefore, that it is useless to provide facilities for young technologists and scientists to receive a course of management training, and then not put them into positions of some responsibility until they are in their middle forties, their training forgotten and their latent ability dulled, if not obliterated, by years of day-to-day routine. It is in this respect that many of the larger industrial concerns fail to avoid one of the weaknesses of Civil Service organisation—the rigid seniority rules governing promotion. A man who has the ability to become a good leader, will be capable of leading at the age of thirty, and the type of man who, at thirty, has the character and energy to accept responsibility is the very type who will experience a sense of frustration if he is not exercised at full stretch during his best years.

In the New Year Honours List

KNIGHTHOOD

ALFRED G. E. BRIGGS, Deputy Controller of Supplies, Ministry of Supply.

HAROLD ROXBEE COX, Chief Scientist, Ministry of Fuel and Power.

ARTHUR CROFT, Chairman and Managing Director, Crofts Engineers (Holdings) Ltd.

LINCOLN EVANS, C.B.E., General Secretary, Iron and Steel Trades Confederation.

CHARLES K. F. HAGUE, Deputy Chairman and Managing Director, Babcock and Wilcox Ltd.

C.B.

J. BUCKINGHAM, Director of Research Programmes and Planning, Royal Naval Scientific Service.

R. SPENCE, Chief Chemist, Atomic Energy Research Establishment, Harwell.

C.B.E.

W. CAWOOD, Deputy Director, Royal Aircraft Establishment.

H. A. CRUSE, Director and General Works Manager, Westinghouse Brake and Signal Co. Ltd.

B. W. A. DICKSON, lately Director and General Manager Vickers-Armstrongs, Ltd. (Aircraft Section).

H. J. POOLE, Chief Superintendent, Armament Research Establishment, Ministry of Supply.

C. A. P. SOUTHWELL, M.C., Managing Director, Kuwait Oil Co. Ltd.

F. V. SPARK, Chief Accountant, Secretary and Director, Harland and Wolff Ltd., Belfast.

H. R. WATLING, O.B.E., J.P., Director, British Cycle and Motor Cycle Manufacturers and Traders Union Ltd.

S. A. H. WHETMORE, lately Joint Managing Director, Billingham Division, Imperial Chemical Industries Ltd.

O.B.E.

B. CURRAN, Director, Edward Curran Engineering Co. Ltd.

N. F. DUKE, D.S.O., D.F.C., A.F.C., Chief Test Pilot, Hawker Aircraft Ltd.

J. O. M. FISHER, General Manager, Humber Graving Dock and Engineering Co. Ltd.

A. GRIFFITHS, Production Director and General Manager, F. Perkins Ltd.

W. K. HALL, Works General Manager, Billingham Division, Imperial Chemical Industries Ltd.

F. G. LOWDEN, Chief Buyer, Cars and Trucks, Ford Motor Co. Ltd.

F. W. N. MURPHY, M.B.E., Superintendent, Royal Ordnance Factory, Swynnerton.

M.B.E.

A. G. BOOTH, Chief Technical Engineer, Humber, Ltd.

J. F. BOOTH, Managing Director, Hepworth Iron Co. Ltd.

T. M. CAMERON, Director, Alexander Findlay and Co. Ltd.

S. DOMVILLE, Works Manager, Curran Steels, Ltd., Cardiff.

A. ELSON, Accident Prevention Officer, Samuel Fox Company Branch, United Steel Companies Ltd.

I. F. FISHER, Works Manager, British Timken Ltd.

F. FLETCHER, Manager, Special Technical Productions, General Electric Co. Ltd.

T. GUTHRIE, Technical Manager, Swan, Hunter and Wigham Richardson Ltd.

J. L. HAMILTON, Personnel Manager, Northern Aluminium Co. Ltd.

F. HERDMAN, Engineer Manager, Gun Mounting Dept., Vickers-Armstrongs Ltd.

J. E. HUMPHREY, lately Senior Executive Officer, Ministry of Materials.

H. S. JONES, Chief Engineer, Round Oak Steel Works Ltd.

H. MOLIVER, Personnel Manager, Craven Brothers (Manchester) Ltd.

B. L. NEWBOULD, Manager, Steel Melting Dept., Thomas Firth and John Brown Ltd.

C. PARKER, Director and Works Manager, Raleigh Industries Ltd.

C. H. C. PAYNE, Construction Designer, Billingham Division, Imperial Chemical Industries Ltd.

J. H. POLSON, Steel Foundry Moulding Shop Superintendent, David Brown Foundries Company.

E. SALTHOUSE, Chief Draughtsman, Electrical Drawing Office, Harland and Wolff Ltd.

E. SAUNDERS, lately Works Manager, Silvertown Works, Imperial Chemical Industries Ltd.

R. SMITH, Head Foreman Electrician, Cammell Laird and Co. Ltd.

W. E. WATSON, Area Works Manager, S. Smith and Sons (England) Ltd.

C. J. WATTS, Chief Draughtsman, Camper and Nicholsons Ltd.

T. S. WOOD, Chief Draughtsman, Electrical Dept., John Brown and Co. Ltd.

B.E.M.

V. A. ALDOUS, Lathe Turner, English Electric Co. Ltd.

F. ASKEM, Electrician, Darwins, Ltd.

S. M. T. BEACH, Foreman, Ferguson Pailin Ltd.

A. BLUNDY, Foreman, Hydraulic Testing Dept., Worthington Simpson Ltd.

A. C. J. CARPENTER, Foreman Shipwright, J. Samuel White and Co. Ltd.

J. W. DITCHFIELD, Foreman Bricklayer, Lancashire Steel Corporation, Ltd.

W. EWART, Foreman Fitter, Harland and Wolff Ltd.

E. GILLON, Machine Tool Setter, David Brown Tractors (Engineering) Ltd.

G. GOLDING, Foreman, John Lysaght (Bristol Works) Ltd.

H. W. HIBBERT, Senior Machine Shop Foreman, Ross Ltd.

C. H. KNOYLE, Senior Artificer, National Physical Laboratory (New Malden).

R. McINTOSH, Maintenance Shop Foreman, Anderson Boyes and Co. Ltd.

W. E. MITCHELL, Technician, Marston Excelsior Ltd.

S. H. NORMAN, Foreman Plate Layer, Guest Keen Baldwins Iron and Steel Co. Ltd.

J. W. ROYLE, Chargehand, Leyland Motors Ltd.

J. STRAUGHTON, Telephonist and Switchboard Operator, Workington Branch, United Steel Companies Ltd.

L. T. SULLIVAN, Foreman, Mullard Blackburn Works Ltd.

D. A. WALLACE, Superintending Foreman, Dumfries Factory, Imperial Chemical Industries Ltd.

W. R. WHITLOCK, Chief Fettler, Bristol Foundry Co. Ltd.

W. A. WILKINSON, Foreman-in-Charge, Scotswood (Newcastle-on-Tyne) Factory, Darlington Insulation Co. Ltd.

Developments in Alloy Steels

A Review of Recent Progress

By C. Sykes, D.Sc., F.R.S.

Thomas Firth and John Brown, Ltd.

The relative scarcity of certain alloying elements has influenced considerably the developments in alloy steels during the last year or two. Not all the work has been directed towards substitute finding, however, and some of the principal items investigated are reviewed here. Although the main emphasis is on the field of corrosion-and heat resisting steels, where the effort has been greatest, reference is also made to high-speed steels, boron steels, and the use of the rare earths as alloying elements.

THE shortage of the principal steel alloying metals, viz., nickel, cobalt, tungsten and molybdenum continues, and although it is not quite so serious as it was a year ago, the need for conservation of these elements, especially nickel, still persists. A large nickel deposit has been discovered in Tanganyika, but work on it is still in an exploratory stage, and the possibilities of the development of tungsten production in Uganda are being explored.

Since, however, there appears to be little immediate prospect of any considerable increase in availability of these short supply metals, steps have been taken to economise in their use. A Technical Committee under the Chairmanship of Mr. H. H. Burton has studied the problem of economy in the use of alloying elements, and as a result several British Standards Emergency Specifications have been issued covering case-hardening steels (B.S. 970, Addendum No. 1, 1951). These are set out in Table I.

Economy has also been achieved in the through-hardening steels by limiting the amounts of nickel and molybdenum according to the size and tensile strength desired.

High-Speed Steels

During the last few years, attention has been given to the high-alloy high-wear type of high-speed steel.[1] These super-high-speed steels are, in general, adaptations of types which have been known for many years, and are characterised by a high alloy content, especially of cobalt and/or vanadium, sometimes associated with carbon contents of up to 1·5%. A study of their micro-hardness[2] showed that carbides in the three high-vanadium high-carbon super-high-speed steels examined are of at least two types. One type is extremely hard, being approximately 2 points Rockwell C harder than tungsten carbide particles found in a plain tungsten carbide compact. The second type carbide is comparatively soft, being approximately 8 points Rockwell C softer than tungsten carbide.

A German investigator[3] used rough-turning as a measure to determine the optimum additions of alloying elements to high-speed steel. Attempts to develop a high-chromium steel were unsatisfactory and steels containing aluminium gave variable results. The use of special nitrides, particularly aluminium nitrides, is of interest. A steel with 2·5–3% molybdenum, 3% vanadium and 2·5–3% tungsten proved to be satisfactory for planing and milling cutters and for twist drills, rivalling steel with 1–1·5% vanadium and 18% tungsten, but its lack of toughness prevented its use for fine drills. A steel with 1·6% vanadium and 9% tungsten is said to be equal to one containing 1% vanadium and 18% tungsten for drilling and milling. Cobalt-containing steels are preferably reserved for heavy turning, where hardness at red heat is required; 3–5% cobalt is usually adequate, higher contents being necessary only for special uses. Steels with high

TABLE I.—EMERGENCY SPECIFICATIONS TO REPLACE THE CASE-HARDENING STEELS EN 33, 34, 35, 36, 37, 38, 39 AND 325.

En No.	Type of Steel	Composition (maxima)								Properties (minima)		
		C %	Si %	Mn %	Ni %	Cr %	Mo %	S %	P %	M.S. tons/sq. in.	El. %	Izod ft. lb.
351	¾% Ni-Cr case-hardening steel ..	0·20	0·35	0·60/1·00	0·60/1·00	0·40/0·80	0·10	0·05	0·05	45	18	30
352	1% Ni-Cr case-hardening steel ..	0·22	0·35	0·50/1·00	0·85/1·25	0·60/1·00	0·10	0·05	0·05	55	15	20
353	1¼% Ni-Cr case-hardening steel ..	0·22	0·35	0·50/1·00	1·00/1·50	0·75/1·25	0·08/0·15	0·05	0·05	65	12	20
354	1¾% Ni-Cr-Mo case-hardening steel	0·22	0·35	0·50/1·00	1·50/2·00	0·75/1·25	0·10/0·20	0·05	0·05	75	12	20
355	2% Ni-Cr-Mo case-hardening steel (low Cr)	0·20	0·35	0·40/0·70	1·80/2·20	1·40/1·80	0·15/0·25	0·05	0·05	85	12	25
361	"15" carbon low alloy case-hardening steel	0·13/0·17	0·35	0·70/1·00	0·40/0·70	0·55/0·80	0·08/0·15	0·05	0·05	45	18	25
362	"20" carbon low alloy case-hardening steel	0·18/0·23	0·35	0·70/1·00	0·40/0·70	0·55/0·80	0·08/0·15	0·05	0·05	55	15	15
363	"25" carbon low alloy case-hardening steel	0·22/0·26	0·35	0·70/1·00	0·40/0·70	0·55/0·80	0·08/0·15	0·05	0·05	65	—	—

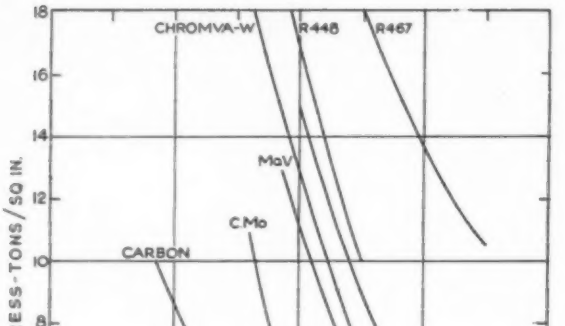


Fig. 1.—Creep values of various steels. The curves represent the stress-temperature relationship for fracture in 1,000 hours.

vanadium content are recommended for tools subject to very heavy wear.

Boron Steels

During the last decade, numerous reports have been published, particularly in the U.S.A., on the effect of small additions of boron on the hardenability of quenched and tempered steels. Further, it has been found[4] that the addition of 0·003% boron to low-carbon 0·5% molybdenum steel in the normalised condition gives double yield strength and a 30% increase in tensile strength, but that the advantage due to boron is very slight when the molybdenum content is less than 0·35%. A more recent claim[5] is that the addition of 0·005–0·1% of boron to steels of the austenitic chromium-nickel type containing, in addition, molybdenum, tungsten and one of the elements niobium, tantalum, vanadium or titanium, improves the high temperature strength.

The possibility of economising in the scarcer alloying elements by the addition of boron has been investigated by the American Iron and Steel Institute, who have recently published a series of tentative specifications for boron-containing steels.

It is estimated that the production of these boron steels in the U.S.A. has now reached a figure of about 50,000 tons per month, and such an output may well suggest that such steels have a practical value.

Previous work on the boron-oxygen equilibrium in liquid iron, and evidence of boron pick-up from the fortuitous presence of borates in furnace linings, had suggested the possibility of adding boron to steel by reduction from a slag containing boric oxide. This has been investigated[6], and it has been shown that boron can be introduced into steel from a borate, and that the boron so added can be made effective in providing the improved mechanical properties of boron steels.

Rare Earths as Alloying Additions

The use of rare earths as alloying additions has been acclaimed in the U.S.A. as one of the major developments in the last two years. It has been demonstrated[21] that the addition of cerium plus aluminium, to carbon and low-alloy steel castings, gives mechanical properties superior to those obtained in corresponding steels in which aluminium or silicon alone is used as deoxidant. Cerium has a two-fold effect on sulphide inclusions in cast iron. It not only acts as a desulphuriser, but any remaining sulphide inclusions are small, globular, and randomly distributed, due to the fact that they are precipitated at an early stage in the solidification process. Tests on carbon steel castings indicate that the cerium addition improves ductility at room temperature, and raises the sub-zero impact resistance, and it is claimed to improve the properties of steel having sufficient alloying element to ensure a fully martensitic structure on water-quenching.

In nickel-containing steel[22], it has been found that variations in the ratio of the individual rare-earth elements, especially of cerium and lanthanum, which are the most widely used, affect the degree of improvement. A rare-earth mixture, known as Lan-cer-amp has been developed which is claimed to give optimum results. It consists of not less than 30% lanthanum, 45–50% cerium and 20–24% didymium and yttrium, with iron and residual salts 10% maximum. It is suggested that the reactions of rare-earth elements with hydrogen and nitrogen may be of considerable significance in explaining their beneficial influence.

Among the most important effects attributed to the rare earths is the improvement of the ductility at forging temperatures of nickel-containing steels, including high-alloy steels and the conventional stainless steels, by the addition of Lan-cer-amp[23].

Data are quoted to show that the presence of a very small amount of rare-earth elements improves the high temperature oxidation resistance of chromium-nickel, chromium-iron, chromium-nickel-iron and chromium-aluminium-iron alloys[24]. The durability, or life, at 1,050° C. of a 0·4 mm. diameter wire of chromium-nickel-iron was increased from 75 hours to 350 hours by the addition of 0·11% of Misch metal, and to 1,100 hours by 0·39%. A comparable effect was produced in a chromium-aluminium-iron alloy. There were also indications that constructional alloy steels treated with rare-earth elements scaled more slowly than untreated steels, and formed a thinner, more closely adherent scale.

Corrosion- and Heat-Resisting Steels

As regards economy in the corrosion-resisting steels, much attention has been concentrated on the 17% chromium stainless irons. These are ferritic high-chromium types of stainless iron, and, although by no means new, they do provide in certain instances an alternative material to the austenitic chromium-nickel type of corrosion-resisting steels. The corrosion resistance of this type of stainless iron approaches that of the austenitic 18/8 steels, but it is less amenable to the forming and welding procedures involved in fabricated work, and its properties require careful study before using it for a particular application.

In the heat-resisting class, considerable use has been made of the heat-resisting properties of chromium, and a material containing 0·06% carbon and about 20% chromium, which possesses excellent resistance to oxidation scaling at temperatures up to about 1,000° C., is used for parts which are not to be submitted to high

stress. Such material can be pressed cold, but there have been a number of practical difficulties. However, a fairly wide use is now being made of the 17 and 20% chromium irons for such applications as television cones, sink units and other pressed parts.

Of recent years, attention has been given to improving the creep resistance of the ferritic stainless steels[7], e.g., R.ex 448 (carbon, 0·1–0·2%; chromium, 10–13%; molybdenum, 0·6–0·9%; vanadium, 0·1–0·2%; and niobium, 0·3–0·6%), whose short-time creep-resisting properties compare favourably with those of the stabilised 18/8 chromium-nickel austenitic stainless steels, but the evidence indicated that the ferritic steel becomes increasingly inferior to the 18/8 type, when times of more than 1,000 and 2,000 hours in the temperature range of 550°–650° C. are involved. Fig. 1 shows the creep resistance of R.ex 448 as compared with stabilised 18/8 chromium-nickel steel, a carbon and various low-alloy steels, and R.ex 467, which is an austenitic steel containing 0·2% carbon, 0·7% silicon, 1% manganese, 9·5% nickel, 14·5% chromium, 2% molybdenum, 2·5% copper and 0·8% titanium. Fig. 2 shows a group of shroud rings in R.ex 448 steel.

Another ferritic steel, containing approximately 13% chromium, to which the carbide-forming elements, vanadium, tungsten and molybdenum are added as strengtheners[8], has the following nominal composition: carbon, 0·2%; nickel 0·7%; chromium, 13%; vanadium, 0·3%; tungsten, 1%; and molybdenum, 1%: it is suitable for service slightly above 540° C. It is claimed that the strength compares favourably with austenitic stainless steels at 540° C. and that high ductility is maintained at elevated and room temperatures after long periods of exposure. The steel is not weakened by sharp notches at 540°, 590° and 650° C.

As a result of investigations on creep resistance and constitution of the H.R. Crown Max. type of steel, having a nominal composition of: carbon, 0·2%; silicon, 1·6%; manganese, 0·4%; chromium, 23%; nickel, 11·5%; and tungsten 3%; it was found that the tungsten content could be reduced without serious detriment to the general properties. When the alloy shortage developed it was decided that for certain applications the tungsten content of the H.R. Crown Max. type of steel could be reduced without affecting service performance and H.R. Crown 1, containing less than 1% tungsten, was adopted for centrispun castings for use in aircraft. Fig. 3 shows a selection of centri-die and centrifugal castings for gas turbine and turbo-jet engines in H.R. Crown 1. H. R. Crown Max. is still used for certain precision cast blades where the conditions are extremely critical.

Fig. 2.—A group of shroud rings in R.ex 448 steel.

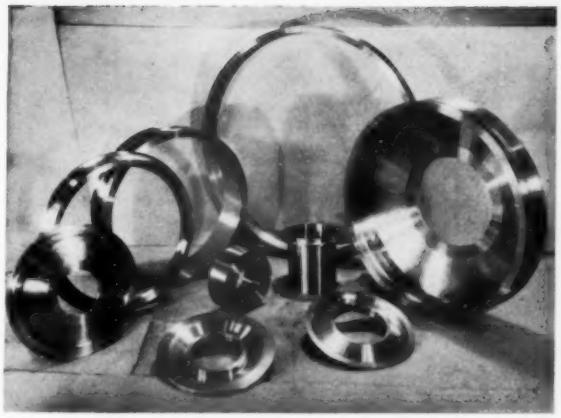


Fig. 3.—A selection of centri-die and centrifugal castings for gas turbine and turbo-jet engines in H.R. Crown 1.

Niobium Steels

A steel containing approximately 0·25% carbon, 17% nickel, 16% chromium, 2·5% molybdenum, 7% cobalt and 1·8% niobium, has been developed which possesses improved creep resistance as compared with previous austenitic steels, combined with good creep ductility and excellent forging properties. Fig. 4 shows a group of disc forgings in this steel, and Fig. 5 shows the world's largest austenitic steel rotor shaft which is produced in this same material.

It has been urged in the U.S.A. that in view of the strategic importance of niobium, alternatives should be sought for all applications in which it can be satisfactorily replaced. Comparison has been made[9], therefore, between the properties of austenitic chromium-nickel steels stabilised (*a*) with niobium and (*b*) with titanium, and it has been concluded that in many cases, titanium-stabilised steel can advantageously be used.

Similar work has been carried out in this country, but the position has not been nearly so critical on account of the fact that titanium-stabilised 18/8 forms the bulk of the production of stabilised 18/8 steels in the U.K.

Further, the American Society for Testing Materials Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys has considered[10] the modification of specifications for austenitic steels, to permit, as far as possible, the conservation of relatively pure niobium, by the use of a niobium-tantalum mixture.

It is pointed out that there are, as yet, insufficient data regarding the properties of the steels over the full range of such additions, from almost total niobium on the one hand to almost total tantalum on the other, but that there is some indication that two types of addition may emerge (especially in respect to the niobium-tantalum ratio), one being principally for use in materials for high temperature service, and the other for corrosion-resisting materials.

Fig. 4.—A group of disc forgings in 326 steel.

Sigma Phase

The sigma phase has been the subject of several recent investigations. A survey of the chromium-cobalt-nickel phase diagram[11] was made by means of microscopic and X-ray diffraction studies on a number of vacuum-melted alloys, and at 1,200° C. the following phases were found: (*a*) a very extensive face-centred-cubic solid solution, based on the binary cobalt-nickel solid solutions; and (*b*) brittle sigma solutions, based on the chromium-cobalt sigma phase which is isomorphous with the iron-chromium sigma phase. The brittleness of the alloys consisting essentially of the body-centred-cubic phase was correlated with the plate-like precipitate of sigma-phase in these alloys.

In the second part of this investigation[12] iron was used as the fourth element, in order to include the commercial alloys based on this quaternary system, and a study of the cobalt-chromium-iron system was also made.

The extent of the alpha-solid-solution field at 1,200° C. in the chromium-cobalt-nickel-iron quarternary system was studied at 10, 20 and 30% iron contents. With increasing iron, the solubility of chromium in the alpha phase decreases, but the chromium-cobalt-nickel ratios remain nearly the same. The martensitic transformation observed in ternary cobalt-chromium-iron alloys was also found in quaternary cobalt-chromium-iron-nickel alpha-phase-boundary alloys. As the iron content in the alpha-boundary alloys of the quaternary system was increased, the nickel content required to suppress the transformation decreased. Transformation in quaternary alloys containing 10% iron was suppressed by 13–18% nickel, and in alloys containing 20 and 30% iron, by 8–13% nickel.

The effect of varying carbon content (0·06–0·29%) on the occurrence of sigma phase in a 25/15 chromium-nickel steel reheated at 700° and 900° C., after initial solution treatments at temperatures within the range 950°–1,250° C., has been examined[13]. It was found that increasing carbon in this type of steel decreased the amount of ferrite in the structures obtained by solution treatment at temperatures between 950° and 1,250° C. after soaking for 4 hours. The ultimate result of increase in carbon was to produce completely austenitic structures at the highest temperature, 1,250° C. The structures obtained in the steels after solution treatment were: (*a*) austenite and ferrite in steels containing 0·06 and 0·09% carbon, solution treated at 1,050°–1,250° C.; (*b*) austenite and carbide in steels containing 0·19 and 0·29% carbon, solution treated at 950°–1,150° C.; and (*c*) austenite in steels containing 0·19 and 0·29% carbon, solution treated at 1,250° C. Sigma phase formed in all three of these structures after prolonged reheating at 700° and 900° C. With increase in carbon content and rise in solution-treatment temperature, the beginning and development of sigma phase was slower, and the mode of occurrence was governed by the structure of the steel resulting from the initial solution treatment.

A study has been made of etching reagents suitable for the detection of sigma phase in high alloy chromium-nickel-iron alloys[14], and it was observed that the modes of attack of the respective solutions varied considerably, e.g., Vilella's hydrochloric-picric acid reagent dissolves the austenitic matrix rather more rapidly than either the carbides or the sigma phase, which stand out in relief against the background, whilst with oxalic acid, used electrolytically, sigma phase and carbides are attacked before the matrix.

During an investigation of sigma phase in nickel-vanadium alloys[15], transitions were observed in the chromium-manganese sigma phase at 1,005° C. and in nickel-vanadium sigma phase at a temperature below 800° C.[16].

A research on the chi phase[17] and its relation to sigma phase has been reported and it is concluded that its occurrence is contingent on the presence of molybdenum. The chi phase has not been found in any molybdenum-free steels.

Chi phase gives an X-ray powder pattern which is closely similar to that obtained with alpha-manganese, and the lattice parameter is generally in the region of 8·86 kX. Attempts to identify the phase microscopically have failed to differentiate it from sigma phase. It is not clear whether the chi phase is a modification of the sigma phase, but it is without doubt closely related to it, and occurs as an alternative in a manner which suggests analogy with transformations characteristic of cobalt. It is considered that the discovery of the chi phase has made some contribution to our knowledge of the sigma phase.

The complex diffusion processes involved in the approach to equilibrium of a high-alloy valve steel, containing 0·45% carbon, 24% chromium, 5% nickel, and 2·5% molybdenum, at temperatures up to 1,150° C. have been studied[18] by examining the microstructural changes produced by heat treatment at several temperatures. The alloy consists of equal proportions of δ-ferrite and austenite, with undissolved chromium carbides occurring mainly in the austenitic zones. Heating at temperatures between 650° and 900° C. causes the sigma phase to form primarily from the δ-ferrite. Maximum hardnesss is attained between 750° and 850° C. The formation of sigma phase is accompanied by complex diffusion processes leading to the transformation of δ-ferrite to austenite (γ^1) at the hardening temperature, and to the transformation of the original and new austenitic phases to α-ferrite on quenching. A secondary hardening effect was observed at 300°—600° C., at a maximum between 475°–500° C., although sigma phase could not be detected in any of these samples. The mode of this 475° C. hardening was different from that observed at 650°–900° C., and an over-ageing effect was found at 550° C.

The occurrence of sigma phase in ferrite-free 25/20 chromium-nickel bar steels has been investigated[19], particular attention being paid to the effect of variable grain size arising from different annealing temperatures. It was found that as much as 10–15% of carbide and sigma phase may be present in fine-grained steels without serious loss of tensile ductility, but moderate grain coarsening, such as might arise from a 100° C. difference in the prior-annealing temperature, will result in the almost complete loss of tensile ductility and impact resistance in the presence of the same amount of sigma phase.

Austenite and sigma phase were extracted[20] by selective anodic dissolution. Extracted sigma phase is ferromagnetic at low temperatures, is richer in chromium and molybdenum and poorer in nickel and iron than austenite, and has a low manganese content. It is also more noble than the corresponding austenite and has a greater tendency to remain or to become passive.

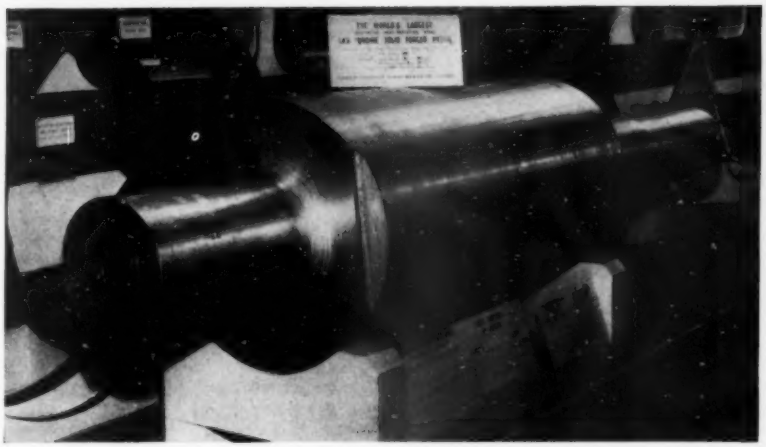


Fig. 5.—The world's largest gas Austenitic steel turbine rotor shaft in 326 steel.

Nickel

The effect of nickel on the stability of austenitic steels has been studied by two French workers[25] who, taking a series of steels containing 18% chromium, and nickel varying between 4 and 12%, determined the proportion of alpha phase formed by cold working. The results have shown marked differences in steels of only slightly different composition, and have confirmed the preponderant effect of nickel in favouring gamma-, and inhibiting alpha-formation.

In an extension of the work[26] on the same series of steels, it was found that for steels heated at 870° C. for 24 hours and cooled at the rate of 300° C. per hour, the Ar ''' point was lowered by about 50° C. for each additional 1% of nickel.

Corrosion Resistance

Certain factors which influence the resistance of normally heat-treated unwelded 18/13/1 chromium-nickel-niobium type steel to boiling 70% nitric acid have been examined[27]. The presence of intercrystalline penetration appears to be characteristic under these conditions, even with steels effectively stabilised against ordinary carbide precipitation effects. Development of a shallow network of intercrystalline penetration is considered to contribute to initial increase in rate of attack with time, and large-grained structures can make this effect more serious. Purity of acid also influences the rate of attack, for example, by small additions of hydrofluoric acid, and metallic contamination from dissolved steel.

A method has been devised for evaluating the corrosion resistance of various materials to phosphoric acid and it has been shown[28] that the presence of copper ions in solutions has an inhibiting effect on stainless steels and that a definite minimum quantity of copper is necessary to achieve this effect.

An investigation on the resistance of metallic materials to corrosion by fluorine at elevated temperatures is reported[29]. The materials exposed included a number of metals and non-ferrous alloys, together with various types of martensitic and austenitic nickel-chromium steels, Armco iron, and carbon steels of various carbon and silicon contents. Temperatures of exposure were varied over the range 200°–700° C.

The results relating to the ferrous materials indicate that none of the stainless steels tested is suitable for handling fluorine at temperatures above about 250° C. Carbon steels containing less than about 0·01% silicon are resistant up to approximately 400° C., but higher silicon materially increases the rate of corrosion, and it is believed that the silicon content of stainless steels may also be partially responsible for their poor resistance to corrosion. Above 400° C. all the carbon steels are attacked too rapidly to make them useful for this type of service.

Intergranular Corrosion of Stainless Steels

The phenomenon of intercrystalline corrosion of the unstabilised 18/8 chromium-nickel austenitic stainless steels is well known. Certain of the ferritic stainless chromium steels, i.e., the steels of the stainless-iron type containing 17–20% chromium, after welding also show this susceptibility to intercrystalline corrosion. In these ferritic steels, however, the attack differs slightly from that of the austenitic steels. In the purely austenitic steels the attack is in the critically heated zone some distance from the weld itself, whilst in the ferritic steels it occurs adjacent to the weld. The reason for this difference in the position of the zone of susceptibility has been studied by German workers.[30] This investigation has been carried out on stainless steels containing 15–30% chromium, with and without varying additions of molybdenum, silicon, aluminium, phosphorus, titanium, tantalum, niobium and vanadium, after quenching from temperatures of 700°–1,350° C., tested in the usual sulphuric acid–copper sulphate solution for tendency to intercrystalline corrosion. These workers concluded that resistance to intercrystalline corrosion is attained only with carbon contents as low as 0·01%, such steels having been decarburised and denitrogenised in hydrogen prior to quenching.

It would appear from work carried out in the U.K., but as yet unpublished, that the susceptibility to inter-

crystalline corrosion of high-chromium ferritic steels, e.g., 17–20% chromium irons, is analogous to that of the unstabilised austenitic steels in that chromiferrous ferrites are capable of dissolving carbides at high temperatures. On cooling, the carbide is spontaneously precipitated and extremely fast cooling rates are required for its suppression. Additions of titanium considerably improve the resistance to this phenomenon, (*a*) by reducing the effective carbon and (*b*) by modifying the solubility characteristics.

Whether the intercrystalline corrosion susceptibility is associated with chromium impoverishment has not yet been determined but the analogous behaviour with austenitic steels would lend support to this theory.

REFERENCES.

1 Leckie-Ewing, P. *Iron Age*, 1950, December 7th, 115–118.
2 Leckie-Ewing, P. *Transactions of the American Society for Metals*, 1952, **44**, 348–362.
3 Scherer, R., and Connert, W. *Stahl u. Eisen*, 1950, **70**, October 26th, 984–994.
4 Bardgett, W. E., and Reeve, L. *Journal of the Iron and Steel Institute*, 1949, **163**, November, 277–294.
5 Binder, W. O. U.S. Patent 2,562,854.
6 Speight, G. E., *Journal of the Iron and Steel Institute*, 1952, **171**, June, 147–153.
7 Kirkby, H. W. *Metal Treatment and Drop Forging*, 1952, February, 61–66.
8 Gin-Young Chow, J., and Kaufman, D. W. *Iron Age*, 1952, November 6th, 166–169.
9 Tyrrell, J. F. *Metal Progress*, 1950, **58**, July, 63–68.
10 *American Society for Testing Materials, Bulletin*, 1951, No. 177, October, 17–19.
11 Manly, W. D., and Beck, P. A. National Advisory Committee for Aeronautics, Technical Note 2602, February, 1952, 45 pp.
12 Kamen, E. L., and Beck, P. A. National Advisory Committee for Aeronautics, Technical Note 2603, February, 1952, 62 pp.
13 Lismer, R. E., Pryce, L., and Andrews, K. W. *Journal of the Iron and Steel Institute*, 1952, **171**, May, 49–58.
14 Gilman, J. J. *Metal Progress*, 1951, **59**, March, 377, 376B.
15 Pearson, W. B. *Nature*, 1952, **169**, May 31st, 934.
16 *Ibid.*, 1952, **169**, January 12th, 70.
17 Andrews, K. W., and Brookes, P. E. *Metal Treatment and Drop Forging*, 1951, **18**, July, 301–311.
18 Cina, B. *Journal of the Iron and Steel Institute*, 1952, **171**, July, 229–237.
19 Morley, J. L., and Kirkby, H. W. *Journal of the Iron and Steel Institute*, 1952, **172**, October, 129–142.
20 Hoar, T. P., and Bowen, K. W. J. American Society for Metals, 1952, Preprint No. 4, 19 pp.
21 Berry, C. D. *American Foundryman*, 1951, **20**, December, 45–46.
22 Knapp, W. E., and Bolkcom, W. L. *Iron Age*, 1952, April 24th, 129–134, May 1st, 140–143.
23 Post, C. B., Schoffstall, D. G., and Beaver, H. O. *Journal of Metals*, 1951, **3**, November, 973–977B.
24 *Engineer*, 1952, **194**, September 26th, 417.
25 Bastien, P., and Dedieu, J. *Metaux et Corrosion*, 1950, **26**, December, 308–311.
26 Bastien, P., and Dedieu, J. *Metaux*, 1951, November, 423–426.
27 Shirley, H. T., and Truman, J. E. *Journal of the Iron and Steel Institute*, 1952, **171**, August, 354–358.
28 Ebling, H. F., and Scheil, M. A. *Welding Journal*, 1951, **30**, October, 511–518s.
29 Myers, W. R., and Delong, W. B. U.S. Atomic Energy Commission, M.D.D.C. 1465; Declassification date, November 13th, 1947.
30 Houdremont, E., and Tofaute, W. *Stahl u. Eisen*, 1952, May 8th, 539–545.

Correspondence

Silver Alloy Brazing of Stainless Steel

The Editor, METALLURGIA.

Dear Sir,

Certain data and figures have been published from time to time concerning the strength of silver alloy brazed joints on mild steel and stainless steel[1,2,3,4]. A perusal of these references will show considerable divergences between the strengths of butt joints in mild and stainless steel as affected by joint clearances and thickness of brazing alloy. Reference 3 shows that the strength of a silver brazed joint in mild steel is independent of the joint clearance, and the statement is made that this refers to any metals with which the silver brazing material does not alloy to any appreciable extent; this statement is, therefore, extended to stainless steel. Moreover, it is stated that the strength of the joint is no greater than that of the brazing alloy in the cast state. Beatson and Brooker[4] reiterate this statement for mild steel and infer its extension to stainless steel. The strengths of butt joints in stainless steel are shown by Leach to be very markedly dependent on joint clearances, and later work by Coxe and Setapen[2] supports this and confirms that joint strengths obtained are much greater than that of the "as-cast" brazing alloy.

We have recently been examining the factors affecting the strength of butt joints made in stainless steel with silver brazing alloys. Our first experiments revealed widely scattered results, some good, some very bad. Subsequent work is enabling us to isolate the factors and assess their relative importance. As a result of this work, we have developed a technique for producing high strength butt joints and have consistently obtained results beyond the yield point of stainless steel, not only at room temperatures but at elevated temperatures up to 350° C. Room temperature tensile strengths of up to 40 tons/sq. in. have been obtained so far, which is well beyond the strengths of the silver brazing alloys used (approximately 30 tons/sq. in.).

Whereas the present-day technique for producing sound joints in mild steel is well known and highly satisfactory, similar satisfactory results by the same technique are not obtained on stainless steel; thus, a specialised brazing technique is necessary to produce consistent strengths of brazed butt joints.

We intend to publish a detailed account of our work leading up to the high tensile strengths which are obtained by our technique for the silver alloy brazing of butt joints in stainless steel, and of the practical industrial applications attainable on a commercial scale.

Yours faithfully,
R. C. JEWELL,
Metallurgical Director,
The Sheffield Smelting Co. Ltd.

Sheffield.
19th December, 1952.

REFERENCES.

1 R. H. Leach. Several articles in journals about 1935–1936.
2 C. D. Coxe and A. M. Setapen. *Welding Journal*, May, 1949, **28**, 462–466.
3 Ministry of Supply. Memorandum on Brazing—Welding Memorandum No. 9.
4 E. V. Beatson and H. R. Brooker. *Welding and Metal Fabrication*, May, 1952, **20**, 182–188.

Virgin Aluminium Supply

Of the total United Kingdom consumption of virgin aluminium, which amounts to some 200,000 tons a year, The British Aluminium Company produces about 30,000 tons. This material is subject to allocation by the Ministry of Supply, and under a contract which expired at the end of 1952 the Ministry of Materials bought The British Aluminium Companys' output for resale along with imported metal. This arrangement has now been discontinued, and most of the metal produced by The British Aluminium Company will be used in their own works, but they have agreed to continue to supply to other users who require their metal for special purposes, and such sales will be licensed by the Ministry of Supply in accordance with any distribution scheme for the time being in operation. This arrangement will not affect the Ministry of Materials' selling price, and the Company will sell at a price not exceeding the Ministry's current price for imported aluminium.

Copper and Copper Alloys
A Survey of Technical Progress during 1952

By E. Voce, M.Sc., Ph.D., F.I.M.
Copper Development Association

Continued progress has been made during the past year in the metallurgy of copper and its alloys, and in the various sections of this review the author discusses the principal items of interest concerning such subjects as raw material resources, extraction, fabrication, finishing and properties.

IT seems appropriate to open this Survey with a reference to the First World Metallurgical Congress, the Proceedings of which have recently been published.[1] In addition to over 50 technical papers, some of which will be described later, the volume contains several items on metal economics of interest to the general reader.

In the first of these papers, Boyd[2] reviewed in general terms the metallurgical resources of the world and outlined the problems of efficient extraction and effective conservation which confront the modern metallurgist. He instanced the enormous drain on world resources caused by corrosion which was estimated to cost the United States alone nearly £2,000,000,000 a year. In a brief reference to copper production in the E.C.A. countries, van der Rest[3] predicted a moderate increase during the next few years, mainly from Northern Rhodesia and the Belgian Congo, while Williams[4] gave percentages of copper output contributed by various groups of countries. Though his figures do not seem to agree with those available from other sources, they serve to emphasise the relatively low contribution of the Soviet controlled bloc. In the last of the group of papers at present under review, Harten[5] dealt with the conservation of metals and with the substitution of those which are more plentiful for those in relatively short supply. His examples concerning the substitution of aluminium conductors for copper in certain electrical applications are familiar; more intriguing is the suggestion that zinc in brass can be replaced in part by light metals. Presumably he had in mind the use of aluminium and possibly of silicon, and his remark may be construed as a plea for the wider adoption of aluminium and silicon bronzes and brasses as substitutes for the straight copper-zinc alloys. It should be pointed out that, while conserving zinc, such substitution would have the effect of increasing the consumption of copper.

A comparable British Symposium[6] dealt with primary resources of both ferrous and non-ferrous metals, and also with the reclamation of scrap, secondary metals and substitute metals.

The Production of Copper

An important new source of supply of copper, and incidentally of cobalt, is the mine which is now being developed near Kitwe in Northern Rhodesia.[7,8] Production is scheduled to begin in 1956 and it is estimated that, when in full operation, about 16,000 tons of copper and over 200 tons of cobalt will be produced annually. A somewhat similar property at Kilembe in Uganda is also to be brought into production.[9,10,11] Ore reserves are estimated at 15,000,000 tons with a probable overall grade of 2·4–2·5% copper and 0·18–0·20% cobalt. Copper appears to be associated with cobalt, and in this case also with nickel, at the Funter Bay mine in South Eastern Alaska,[12] while copper in addition to nickel and platinum is to be extracted at Rankin Inlet Nickel Mines on Hudson Bay[13] and a new discovery of copper-nickel ore has been made near Mesabi, Minnesota.[14] The Sherritt-Gordon mine, its reserves exhausted, has closed down and much of the equipment is being moved to the newer property at Lynn Lake.[15,16,17,18] Extraction of ore from the mine will probably start late in 1953.

Activity in Scandinavia is shown by the fact that the Boliden Company is at present carrying out an ambitious programme of reconstruction at its Ronnskär copper works in northern Sweden.[19,20] It is claimed that the largest electric arc furnace in the world will soon be located there, to operate on copper. Further information on the Finnish technique of flash smelting has become available,[21] while descriptions of the methods of working the Mansfield deposits[22] and of the Norddeutsche Affinerie[23] in Germany, have also appeared.

In Yugoslavia there is much mining and metallurgical activity, not only at the well established Bor copper mines, but also at the newly found Majdanpek copper deposits of Eastern Serbia.[24,25] The output of the electrolytic copper refinery at the Bor mines is being increased from 14,000 tons to 24,000 tons per annum. The Government of Israel proposes to work a vein of ore estimated to contain 100,000 tons of copper in an area of Southern Negev near the Gulf of Akaba,[26] where there are traces of copper workings dating back to the time of King Solomon. While considerable copper deposits in addition to other metallic ores are known to exist in French Mauritania, a recent appraisal of the situation emphasises the local difficulties of their exploitation.

For some years it has been known that important developments are in progress at the International Nickel Company's plant at Copper Cliff. The flash smelting process is being put into operation for the production of matte from powdered concentrate, and in this connection a large oxygen plant has been installed. The gaseous products of flash smelting consist largely of sulphur dioxide, most of which is liquefied for use in the pulp industry while some is oxidised to sulphuric acid. Allgood[27] describes these processes with the help of flow sheets.

Two suggestions which seem worthy of note concern flotation and electrolytic refining respectively. Investigators in Japan[28] have found that ultrasonic waves can

be used with advantage to facilitate the emulsification of flotation reagents, while Schimmel[29] has explored the possibility of refining copper from ammoniacal electrolytes. His attention was focused on cuprous salts which require only half the electricity needed to liberate the metal from the more usual cupric baths.

Several new ways for the separation of copper from other metals deserve mention. Balint[30] has patented a process for the separation of copper and nickel sulphates. Most of the copper is first crystallised out and the remainder precipitated by the addition of a slight excess of alkali, after which the nickel remaining in solution is worked up by orthodox methods. An apparently more practical technique, developed by the Outokumpu organisation,[31] is based on the direct electrolysis of nickel-copper matte. The aim is to make pure nickel from the original nickel-rich matte, and either copper or a copper-nickel alloy is simultaneously produced. Because the principle of ion exchange has already been used for the recovery of metals from waste waters, proposals have been made[32] for the application of the process to the separation of copper from zinc: it is shown that certain resins are effective for the purpose. From a study of the equilibria between copper, tin and hydrogen chloride it appears that possibilities arise for the complete separation of these two metals in the processing of scrap.[33] The results obtained are also claimed to be of interest in the analysis of tin bronzes.

Reference must be made to a series of processes developed by the Chemical Construction Company, in collaboration with the Sherritt-Gordon interests, for the recovery of pure copper in powder form from ore concentrates as well as from copper scrap, brass scrap or blister copper.[34] Detailed information is not available, but basically the sequence of operations consists of leaching the material to be treated in autoclaves and, after filtering, reducing the solution so obtained at high temperature and pressure in other autoclaves. It is claimed that almost 100% recovery can be achieved, and that the powder produced meets all standards of purity for oxygen-free high-conductivity copper. Similar methods are applicable to other metals such as cobalt and nickel.

On the wider aspects of scrap processing and secondary metals generally, a new book by Thews[35] is to be welcomed. The subject is covered in detail and with great thoroughness.

Foundry Practice

There is no doubt that synthetic resins are finding increasing applications as binders for core and moulding sands in the foundry. A report by an Institute of British Foundrymen's Committee[36] indicates that resins have the advantage of fast curing and are likely to be specially useful in non-ferrous practice, where metal penetration must be prevented and a good surface finish is important, while Dews and Drury[37] emphasise the need for thorough baking of the cores to minimise obnoxious fumes, especially in the case of urea formaldehyde. Both these papers give much detailed information on the technique of using the resins.

Perhaps, however, the most potentially revolutionary contribution which synthetic resins are likely to make to casting technique is in connection with the shell moulding process, which, developed in Germany during the war by Croning, is creating a great deal of interest both in the United States[38,39,40,41,42,43] and in this country.[44,45,46] It can be regarded as a major technological advance, and has been successfully applied to copper-base alloys. In essence it is simple: dry silica sand mixed with a suitable quantity of a thermo-setting plastic is applied to the surface of heated metal patterns. Thus the sand is bonded by the plastic into a coherent shell which is stripped from the pattern, cured by heating for a brief period, and reassembled to form the mould cavity. The assembled mould may be backed with steel shot or with sand if desired, but this is not always necessary[41,42] especially if the castings to be made are small. It is claimed that the shell moulding process offers precision casting at ordinary sand casting costs. The most troublesome stage is the separation of the delicate shell of resin-bonded sand from the metal pattern, and Hoff[47] has recently discussed this aspect and described the use of special oils in a Danish foundry. The patent situation has been to some extent clarified by a statement issued in the United States[39] and reproduced in this country.[46] It would appear that valid patents can now be granted on specific improvements only, and not on the basic process as such. In this country patents[48] by the Polygram Company cover several methods of producing suitable patterns and other details of technique.

As a result of the brass foundry productivity tour,[44] Mantle and Potts[49] suggest that the only important technical point on which there is wide divergence between American and British foundry practice is the extensive use across the Atlantic of aluminium matchplate patterns made by pressure-casting in plaster moulds. Specialist firms make matchplates of high quality so cheaply that they become economic for quite small runs of castings. As a result of experiments in this country, it is considered that individual aluminium patterns as well as matchplates and coreboxes can be successfully produced with British plasters. It is interesting to note that the pressure casting process has been successfully used for the preparation of moulds in beryllium copper for zinc-base diecastings as well as for plastics.[50] Other applications of the plaster moulding technique are described by Pfister.[51]

Another foundry development which, though not new, has lately received experimental attention in this country, is the use of insulating and exothermic sleeves for feeding copper alloy sand castings. As the result of a number of practical trials, Skinner and Ruddle[52] conclude that with special castings where good feeding is imperative but difficult, either insulating sleeves of gypsum or exothermic materials should be of considerable benefit. Examples of the application of exothermic sleeves for knock-off feeding heads are given by Robinson[53] who also deals with the now well-known Connor block or hot lip runner.

Unlike the foregoing, both degassing and the harnessing of the metal-mould reaction are peculiarly British developments in the production of sound castings in bronzes and gunmetals. It is now widely recognised that melts contaminated with gas, especially hydrogen, are prone to give unsound castings, but that hydrogen can be effectively removed by bubbling an insoluble gas such as nitrogen or carbon dioxide through the molten metal before pouring. If, however, feeding is inadequate, shrinkage porosity may arise, and thoroughly degassed metal may, for this reason, fail to yield pressure-tight castings. A little phosphorus added to the melt can generate a small amount of hydrogen when the metal

comes in contact with the moist walls of a sand mould, and the effect of the slight gas porosity thus acquired is to disperse the shrinkage porosity and make it much less harmful by breaking up the channels through the casting. Clearly the process must be kept strictly under control because the absorbtion of much hydrogen in this way would lead again to gross gas porosity. Consequently, mould reaction may become dangerous when casting bronzes containing appreciable quantities of phosphorus. Recent publications on this subject are those of Baker,[54] Rutherford[55,56] and Mantle.[57]

Though phosphorus is a well established deoxidant for molten copper, and is widely used as such in industry, little has been known until recently of the equilibrium which exists between oxygen, phosphorus and liquid copper. An extensive research on this subject has been completed by the British Non-Ferrous Metals Research Association and the results formed an important contribution to the First World Metallurgical Congress.[58]

In discussing the grain refinement of non-ferrous castings, Swinyard[59] indicates that iron acts as a grain refiner in aluminium bronze and high tensile brass, and gives experimental evidence of the grain refining influence of this element on Admiralty gunmetal. He also states that nickel has a similar effect in leaded gunmetals. This is at variance with the work of Colton and Margolis[60] who found that the lead itself had a greater grain refining influence than nickel, and who failed to substantiate the widespread impression that nickel improves the distribution of lead particles in the binary alloys of copper and lead for bearing applications. In the latter connection, Liddiard and Forrester[61] express the view that powder metallurgy, although having problems of its own, eliminates many of the difficulties inherent in the casting of copper-lead.

Several accounts have appeared in the Press of recommended practice for the casting of certain particular copper-base alloys. All who are interested in the casting of high-strength aluminium bronze should study a paper by Hargreaves[62] who expresses the opinion that the greatest single factor contributing to success is the use of exothermic sleeves for the feeding heads. De Pierre and Wynne,[53] and also Vanick,[64] have dealt with the same subject from the American viewpoint. Remarkably full in scope are papers by Grand[65] on the sand casting of beryllium copper, and by Vanick[66] on cupro-nickels. Both of these publications include information on the effects of added elements and impurities.

Against the background of the long series of researches which Pell-Walpole has conducted on the chill casting of phosphor bronzes, a book has appeared under the joint authorship of Professor Hanson and himself.[67] This is far more than a mere record of experimental work carried out under the supervision of the authors; it represents a masterly and comprehensive review of the whole subject and well over 900 references to other publications are made in the text.

This section on foundry practice would be incomplete without mention of a contribution by Dinsdale, of the British Railways Executive, to the recent Institute of Metals Symposium on Metal Economics.[6] At the time of nationalisation, the railway foundries were casting no less than 37 different copper-base alloys. The Executive have now selected five materials to cover all their requirements, thereby greatly increasing administrative efficiency. This desirable move has been discussed elsewhere.[68]

Fabrication

Most readers will already be conversant with the Sendzimir mill, in which the thrust on a pair of small-diameter work rolls is transmitted to the rigid casing of the machine through a series of backing rolls. Considerable advantages in rapidity of production and accuracy of gauge are claimed over the orthodox screw-down type of mill. More recently, Sendzimir[69] has invented a modified machine in which a series of small-diameter work rolls circulate like planets around a pair of larger backing rolls. Thus several pairs of work rolls operate successively on the metal within the reduction zone, and very heavy reductions in a single pass can be achieved. Another novel method of producing sheet and strip is a development of the British Iron and Steel Research Association.[70] The material to be reduced in thickness is bent round a roll while the ongoing and offgoing portions are maintained under a tension less than that required to cause plastic flow. The extra stresses imposed by the bending are then sufficient to cause substantial plastic deformation and reduction of thickness as the material passes over the roll. Comparable in principle is a machine patented by Chappuis[71] for the cold forming of metal blanks. The blank is first subjected to a rapidly increasing pressure to bring the material into the plastic condition. During this stage energy is stored in elastic members of the machine, from which it is then automatically released to complete the deformation of the blank to the required shape.

A remarkably complete description of the production of copper wire, with a bibliography of 50 references, has been published by Rolle[72], while a useful paper by Blazey and Benjamin[73] provides both wire drawers and machine builders with information conducive to efficient use of equipment. MacLellan[74] has developed the mathematical theory of friction in wire drawing, while Wistreich[75] has discussed the wear of wire-drawing dies with special reference to the type of localised wear known as "ringing." He suggests that a panacea might be found by improving lubrication.

It has generally been held that the defect known as "crow's feet," which occasionally appears during the drawing of copper wire, is attributable to the extra cuprous oxide associated with the set surface of horizontally cast tough-pitch wire bars, though some have ascribed it to slight superficial "gassing" when the bars are preheated for rolling to wire rod. A recent careful study of the matter by Ström and Waller[76] has shown that the first diagnosis is almost certainly correct, although, if strongly reducing conditions occur during heating, some cracking attributable to gassing may arise.

Somewhat similar in scope is the work of Ergang and Welz[77,78] on the occurrence and prevention of flow lines during the fabrication of articles from nickel silver and brass strip. The phenomenon is associated with a sharp break in the stress-strain curve of the material at the yield point.

Considerable interest is being shown in the production of clad metals of various kinds, and the methods available have been outlined by Weber.[79] The manufacture of bullet envelopes of steel clad with gilding metal continues[80] and new equipment has been developed to increase production.[81] In this connection experiments have been in progress on the use of a methyl borate flux ("Gasflux"),[82] and the process is said to have passed the development stage and to be available for

commercial use.[83,84] Aluminium sheet clad on one or both sides with copper is now available commercially in this country[85] and composite tubes of various metals are obtainable from several sources. New methods of coating copper and steel with lead have been developed in Germany and are in use in the United States[86] while the British Non-Ferrous Metals Research Association has been granted a patent[87] covering small additions of nickel to lead for coating the same metals. Applications of lead-coated copper include gas water heater units, car radiator blocks, coiled piping for chemical processes and insoluble anodes for chromium plating. Steel clad with copper also has important applications in chemical engineering,[88] building, and hardware,[89] while copper clad with stainless steel is valuable for service at elevated temperatures,[90,91] including those of gas turbines.[92]

The annual Symposium of the Institute of Metals was this year concerned with thermal treatment. Only one of the seven papers presented, namely that by Davis and Temple,[93] dealt directly with copper-base materials, though two others[94,95] gave valuable information on electric furnaces and gas equipment respectively for general use in the non-ferrous industry. The paper by Davis and Temple presents a remarkably clear and comprehensive picture of the heat treatment of copper and copper alloys, while to supplement the information given in the other two, readers may find it helpful to study an article[96] in which many individual furnaces are named and described. Jenkins[97] emphasises the advantages of high-frequency heating in the forging industry.

Finishing and Plating

Shortage of nickel has recently led to the development of alternative electrodeposited coatings, especially for use beneath chromium. Of these, white brass,[98,99] bronze,[100,101] and a ternary alloy of copper, zinc and tin,[102] seem to rank among the more promising, while a bright copper deposit from an acid solution can also be used, with or without a flash of nickel, beneath the chromium surface.[103] Both Chadwick[104] and Miller[105] presented papers at the Summer Conference of the Institute of Metal Finishing on the electrodeposition of chromium directly upon copper and copper alloys. Comparable in object is a process which is claimed to give a white surface on copper and copper alloys without electrodeposition of any other metal.[106,107]

In reviewing the intensive development work which has been carried out in America on periodic reverse current (PR) plating, Halls[108] mentions quite phenomenal mechanical properties which may be obtained for copper electrodeposited by this method. Based on statements by Jernstedt,[109,110] he quotes tensile strengths of up to 50 tons/sq. in. with elongations of about 9% and hardness values of the order of 220 diamond pyramid number.

Electrodeposited copper is well known as a " stop-off " in the case hardening of steel, and normally gives excellent results for this purpose. Ruffle and Chawner,[111] however, report instances in which the effect of the copper in preventing access of the carbon to the steel appeared to spread slightly beyond the confines of the plated area, thus leaving parts soft which should have been hardened. The authors traced this to the presence of small quantities of barium sulphide in the barium carbonate of the carburising compound. In the nitriding, as distinct from the carburising, of steel it is said that electrodeposited bronze containing 10–15% of tin has largely superseded tin plating as a " stop-off " medium.[112]

An interesting development is the production of fine mesh metal gauze by electrodeposition upon textile fabric,[113,114] while a careful experimental study[115] of the mechanism of electrolytic polishing is to be welcomed.

Properties and Applications

Perhaps because the ordinary tensile properties of copper at elevated temperatures are of less practical importance then creep, little attention has been paid to this subject for many years. Recently, however, Munse and Weil[116] have published the results of an extensive series of mechanical tests on electrolytic tough pitch copper, OFHC copper, and a material described as " deoxidised high-phosphorus copper," at temperatures ranging from −196° to 204° C., and upwards to 649° C. in the case of the deoxidised copper. On the whole, the three types of copper behaved very similarly to each other. Russell[117] has carried out tests on copper and aluminium after exposure in air for one year at 150° C. and for nine months at 260° C. to determine their relative suitability for electrical conductors at temperatures which might be encountered with new types of insulation. Oxidation was not an important factor for either metal at 150° C.; at 260° C., however, copper scaled appreciably whereas aluminium did not. On the other hand the tensile strength of the aluminium was reduced to a much greater extent than that of the copper. After reviewing the literature of indentation hardness tests on pure metals at elevated temperatures, Westbrook[118] concludes that the relationship between hardness and absolute temperature can be expressed by a simple exponential equation.

Though the complex aluminium bronze containing approximately 10% of aluminium, with 5% each of iron and nickel, is recognised to be among the toughest and strongest of the copper-base alloys, the changes of structure and properties which can be brought about by heat treatment have heretofore been little understood. Much of the obscurity has now been dispelled by the work of Cook, Fentiman and Davis[119] who examined the structure and properties of such alloys in the wrought condition. Numerous test results are given in the paper for various conditions and compositions. Similar in object, though less comprehensive in scope, is the work of Kasberg and Mack[120] on a 12·3% aluminium bronze containing 3·7% of iron with small amounts of nickel and manganese, a type of material which is used for gears, bearings and parts subjected to wear. It was found that the modulus of elasticity could be varied by heat treatment over a considerable range. A careful investigation of the creep and fatigue properties at 500° C. of two α-aluminium bronzes has been reported by Carter, Mends and McKeown.[121] Both materials underwent structural changes on holding at 500° C., and resistance to oxidation was less satisfactory under condition of cyclic stress than it promised to be from tests in the unstressed condition. Fatigue and corrosion fatigue tests by Sopwith[122] on a straight 9·3% aluminium bronze and on beryllium copper, both in the heat-treated condition, indicated that neither material behaved so well after heat treatment as previous tests[123] in the extruded and drawn condition had promised. A recent patent[124] claims that the addition of up to 0·3% of beryllium to the cast aluminium bronzes inhibits the formation of entrapped alumina

skins in the castings and improves their mechanical strength.

Richards[125] has surveyed over 90 recent literature references on the properties of beryllium, copper-beryllium and other beryllium alloys. Other publications with which this author is associated record original work on the properties[126] and uses[127] of beryllium-copper wire and the cold-forming characteristics of beryllium-copper strip prior to heat treatment.[128] By X-ray diffraction Geisler, Mallery and Steigert[129] have identified three distinct precipitates which appear with increasing time of ageing of the 1·7% beryllium-copper alloy at 300° C., and possibly this may in part account for the variation in properties which is sometimes encountered between different batches of commercial beryllium copper. Further light may also be thrown on this problem by a study of segregation in a copper alloy containing 1·82% of beryllium by Gruhl and Wassermann.[130]

Not long ago, Bailey[131] published an extensive account of the research and development carried out by the British Non-Ferrous Metals Research Association leading to the introduction of the modern iron-bearing cupro-nickels for the tubing of marine condensers and other applications involving sea water corrosion. Much interest in these alloys is now being evinced by naval and other dockyards, not only in this country but also in the United States where Palmer and Wilson[132] have published a paper which is similar in scope to that of Bailey.

Though not practised extensively in this country, Continental manufacturers frequently add small amounts of phosphorus to cartridge brass, chiefly with the object of restricting grain growth during annealing. Meikk-Oja[133] has shown that the efficacy of phosphorus in this direction is considerably influenced by the iron content of the material. Sinclair and Craig[134] have critically examined the effect of grain size on the mechanical properties of 70/30 brass.

The well-known hardenable copper-nickel-manganese alloys have been further developed according to several Canadian patents. These refer to copper alloys containing up to 25% each of nickel and manganese, together with smaller additions of silicon,[135] aluminium[136] or these two elements together.[137] Copper-nickel-phosphorus, already established as a precipitation-hardening alloy of high electrical conductivity, has been made more easily machinable by the addition of tellurium.[138]

During the past few months, researches have been published on the constitution of a number of alloy systems containing copper, including those of certain of the rarer elements. The advent of titanium as an industrial metal makes determinations of the copper-titanium phase diagram by Karlsson[139] and by Joukainen, Grant and Floe[140] particularly opportune. Hume-Rothery and his collaborators have studied the copper-gallium[141] and copper-indium systems,[142] but in neither case were the copper-rich alloys investigated. The same remark applies to a paper by Basinski and Christian[143] on manganese-copper alloys. In contrast, the work of Greenfield and Raynor[144] on the ternary copper-zinc-germanium alloys was confined entirely to the copper-rich corner of the diagram. Klepps and Weil[145] have studied the solubility of copper in molten lead and the shape of the liquidus curve between 950° C. and the eutectic temperature of 326° C., while Kamibayashi[146] claims that dilute copper-zirconium alloys can be produced by the inward diffusion of electrodeposited zirconium at ordinary temperatures. The constitution of the copper-silver-indium alloys has been examined by Gebhardt and Dreher[147] and that of the copper-nickel-magnesium system by Köster[148] while Allen, Schofield and Tate[149] have reported that the mechanical properties of the copper alloys with zinc, gallium, germanium and arsenic respectively, appear to be almost entirely governed by their electron-atom ratios. Hargreaves[150] has examined the X-ray structure of certain of the copper-nickel-iron alloys, as well as their magnetic and mechanical properties. He was, however, mainly concerned with compositions outside the usual commercial range.

Corrosion and Protection

Reference has already been made to the iron-bearing cupro-nickels which have been developed to meet the stringent requirements of marine condenser tubes and similar maritime applications.[131,132] Much information on the resistance to corrosion of the alloys in question is given in the papers mentioned; nevertheless Stewart and La Que[151] have published an excellent review of the present position from the corrosion angle, attention being directed primarily to the alloys containing 10% of nickel. It appears that nearly 1,000 tons of the material have already been put into service in the United States, and that the record of performance has been good.

Risbridger[152] summarises the results of tests on brasses used for ball-valve seats and concludes that chlorination of the water increases the attack on cast α-brass as well as on hot-pressed $\alpha + \beta$-brass. This finding is somewhat at variance with previous work by Ingleson, Sage and Wilkinson,[153] and also with that of Bulow[154] who suggests that regular chlorination of water flowing through aluminium-brass condenser tubes tends to inhibit dezincification.

According to Clenny,[155] the occurrence of stress corrosion in high tensile brass has led to its replacement, for some items of electrical gear, by aluminium bronze. He adds, however, that even the aluminium bronzes are not completely immune. In this connection it is interesting to note that contact with nylon in tap water has been found to cause stress corrosion cracking of an aluminium bronze containing 5% of aluminium.[156] The effect appears to be attributable to the slow release of ammonia from the nylon.

Kaneda[157] reports that a solution containing 0·6g. of chromic acid and 5 ml. of concentrated sulphuric acid in 95 ml. of water is a preferable reagent to ammonia in assessing the susceptibility of high tensile brasses to stress corrosion cracking, while Lissner[158] has developed a test for stress corrosion in copper alloys which involves immersion in ammonia solution at 80° C. According to Bulow,[159] attempts to inhibit aluminium brass and other brasses from stress-corrosion cracking by treating them with an acidic solution of sodium dichromate proved unsuccessful.

In dealing with the selection of alloys to resist corrosion in oil refineries, Morton[160] differentiates between plant operating at above and below 260° C. For applications in the lower temperature range, copper-nickel alloys are stated to be among the most satisfactory. The corrosive effects on iron and copper of nine motor gear oils, some of them chlorinated, have been studied

by Bukoweicki[161] who found that copper was comparatively heavily attacked: comparable results were obtained by Sawyer.[162] From the practical viewpoint, however, these findings need cause no undue alarm, for little or no trouble is normally encountered with copper-base bearing alloys in respect of corrosion.

Recent papers on protection against corrosion include a study of the leaching rate of antifouling compositions based on cuprous oxide as the toxic component,[163] the relative efficiency of sodium benzoate and other soluble benzoates as corrosion inhibitors when impregnated in wrappings for copper and brass among other metals and alloys,[164] and the use of various solder coatings to protect copper gas appliances from attack by the products of combustion.[165] A paper by Parker[166] describes the attack on brass by types of bacteria which produce ammonia from organic matter, and outlines preventive measures.

Joining

The welding of copper by the argon-arc process has been compared with oxy-acetylene bronze welding.[167] The results obtained were in conformity with those which might have been expected; thus joints in deoxidised copper were usually superior to those in tough pitch or OFHC material. The technique of welding deoxidised copper by the oxy-acetylene method is described in minute detail by Galton,[168] who gives a great deal of practical advice to users of this process. A report of tests comparing the use of a nitrogen-shielded arc with the argon-arc welding of copper has reached this country[169]; it would appear that a higher gas pressure is needed but that the arc power, and consequently the speed of welding, can be increased.

It is stated that the Armco Steel Corporation have solved the problem of copper brazing stainless steel by electroplating the latter with a thin layer of iron, thus permitting the use of orthodox techniques,[170] while from a foreign source comes a description of the pressure butt welding of copper to aluminium by the local formation of the copper-aluminium eutectic at the interface.[171]

In connection with soldering, brazing and hot dip coating, Bailey and Watkins[172] have studied the factors which control the flow of liquid metals over solid metal surfaces. Their results emphasise the importance of the contact angle between the solid and liquid surfaces.

Physical Metallurgy

Until the advent of electrostatic methods of inducing and recording vibrations in metallic specimens, it would have been deemed impracticable to investigate thermal transformations by examining the attendant changes of elastic modulus. Now, however, this procedure has taken its place among research methods, and has been applied to aluminium and tin bronzes.[173] The results obtained were in accord with the accepted equilibrium diagrams.

Metallography, which normally provides qualitative information alone (except in respect of grain size), has recently been applied on a quantitative basis to the re-determination of the copper-zinc equilibrium diagram in the vicinity of the β-phase.[174] No change of slope was detected in the $\alpha + \beta$-/β-phase boundary at the temperature of the order-disorder change, which is thermodynamically peculiar, especially if, as concluded by Rhines and Newkirk,[175] order-disorder transformations are to be regarded as orthodox phase changes.

Studying the recrystallisation and grain growth of cartridge brass during annealing, Channon and Walker[176] deduced certain empirical relationships between the grain size before and after recrystallisation and the degree of deformation to which the material was subjected.

By thermodynamical methods, Chiche and Dode[177] have determined the heats of formation of cuprous and cupric oxides, while from the wider viewpoint the new monograph by Lumsden[178] on the thermodynamics of alloys is much to be welcomed.

Powder Metallurgy

An experimental study on a laboratory scale of the production and properties of oxide-reduced copper powder has been recorded by Ellwood and Weddle.[179] The mechanical properties of objects sintered from the oxide-reduced powder were not greatly different from those prepared from commercial electrolytic and atomised grades, but the flow qualities of the powder itself were inferior.

Butler and Hoar[180] have demonstrated the interesting fact that, though interdiffusion and sintering can and do occur together during the processing of copper-nickel compacts, they are not interdependent. From a somewhat similar research on copper-zinc compacts, Howat, Craik and Cranston[181] conclude that, in sintering under reduced pressure, zinc is first transferred to the surface of the copper particles, whence it diffuses inwards. Until recently, brass has been regarded as a somewhat intractable material in industrial powder metallurgy, nevertheless it is now being used for practical purposes.[182]

Attention is directed to several publications concerned with the infiltration of molten copper into porous iron. It is claimed, for instance, that it is possible to mass-produce gas turbine compressor blades having a yield strength of 40 tons/sq. in. by this means,[183] and that the pressings are able to withstand three or four times as much vibration as stainless or carbon steel blades. Goetzel[184] has described infiltration metallurgy generally, while both Lenel[185] and Stern[186] report the results of experimental work relating specifically to copper and iron.

Somewhat similar in character is a patent[187] for the production of bearings from fabric knitted from a wire of a relatively hard metal such as copper, embedded in a relatively soft matrix of an antifriction metal. Other patents are concerned with the impregnation of wire mesh or wool[188] or porous sintered metal[189] with polytetrafluoroethylene, which has a remarkably low coefficient of friction.

Factors governing the production by rolling of sintered strip from copper, brass and iron powders are described by Naeser,[190] while Primavesi[191] has patented a method for obtaining electrolytic copper powder from anodes of almost any copper-bearing material, such as copper or brass scrap, copper matte or even copper ore.

Analysis and Testing

The issue of B.S.1800 and B.S.1825 covering the chemical analysis of the various British Standard raw coppers and of cadmium copper respectively, marks the culmination of a great deal of careful experimental work and correlation of results between different laboratories. No procedure for the determination of oxygen in tough pitch coppers has been included in B.S.1800; this matter is still under consideration.

A book dealing comprehensively with the chemical analysis of electroplating and related solutions has been published by Langford[192] on the basis of his personal experience, and a new and enlarged edition of Twyman's well-known book on metal spectroscopy[193] has appeared.

Lately a marked change has occurred in the scope of spectrographic analysis. From being confined to the estimation of impurities in small concentrations, its applications have now been extended to the determination of the major alloying elements. In this connection Schatz[194] has published detailed procedures for zinc, lead and iron in copper and copper alloys including the leaded brasses, while Hans[195] has described results obtained on the determination of zinc in brass by means of a direct-reading spectrograph.

Murdza[196] has reported an extensive series of trials by six laboratories to assess the influence of speed of testing on the tensile values of copper-base alloys. Within the range of speed normally encountered in test houses, no significant effect was found.

During the necking of a tensile specimen, the stress system is complicated by radial stresses which are brought into play by the necking process. Some time ago Bridgeman proposed a mathematical correction for this effect based on the radius of curvature of the neck profile, and Marshall and Shaw[197] have shown this to be valid for copper and steel. Their technique of testing with the help of a jeweller's ring gauge offers a new method of determining true stress-strain curves for use in cold-working operations.

The use of simple hot-forging tests to predict behaviour in hot rolling and other industrial hot-working processes has attracted the attention of metallurgists for many years. Simmons[198] reports that such tests correlate well with the relative plasticity of copper-base alloys under hot rolling, but that they fail to reveal the hot shortness exhibited by some of the materials.

Another subject which has exercised research workers for a considerable period is the correlation of creep data obtained under constant load or stress with stress relaxation at constant strain. This matter is of interest in connection with such practical problems as the "shortening" of the copper windings of large alternators, and a recent theoretical discussion by Roberts[199] is therefore to be welcomed. The author includes experimental work on copper at room temperature and at 165° C.

Miscellaneous

An interesting lecture by Teed[200] on metals in relation to stratospheric flight emphasises the problem of the rapid wear which occurs on commutator brushes of electrical machines operating at high altitudes. It would appear that the solution of the difficulty must be sought in modifying the carbon of the brushes rather than in the type of copper or copper alloy used for the commutator segments themselves.

Two papers in the *Journal of Chemical Education* give instructive accounts of metallurgical practice in the bronze age of ancient Syria,[201] and of the alloys of gold and copper known to the peoples of Colombia before Colombia itself was known to the peoples of Europe.[202]

A useful book on electrical contacts has appeared[203] and it is a pleasure to note the new, revised edition of the excellent Penguin "Metals in the Service of Man."[204] According to Freeman[205] copper has been in service on the roof of a church in Philadelphia for 213 years. Recent inspection and tests have shown it to be in excellent condition and likely to serve for many years to come.

REFERENCES.

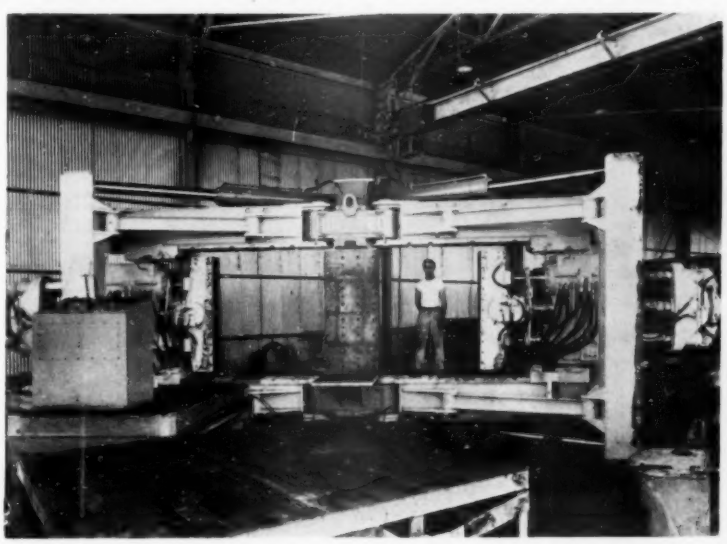
1 Proceedings of the First World Metallurgical Congress, 1951. *American Society for Metals.*
2 *Ibid.*, 82.
3 *Ibid.*, 91.
4 *Ibid.*, 100.
5 *Ibid.*, 113.
6 Metal Economics (Symposium). *J. Inst. Metals*, 1952, **80**, 225-254.
7 Anon. New Copper and Cobalt Mine in Northern Rhodesia. *World Mining*, 1951, **4**, 57.
8 Anon. Copper and Cobalt from Northern Rhodesia. *Chem. Age*, 1951, **65**, 263.
9 Anon. Many Millions will be Needed for Ventures African Project. *Northern Miner*, 1951, June 14th, 15.
10 Anon. Uganda: Kilembe Development. *World Mining*, 1952, **5**, May, 53.
11 Anon. Production Closer for Kilembe Mine. *Northern Miner*, 1952, January 31st, 16.
12 Anon. Alaska—Nickel Cobalt. *Mining World*, 1952, February, 60.
13 Anon. Planning More Work at Rankin Inlet Nickel Mines. *Northern Miner*, 1952, **38**, April 17th, 8.
14 Anon. Nickel-Copper Discovered Near Mesabi-Vermillion. *Eng. and Min. J.*, 1951, **152**, 102.
15 Charlewood, G. H. Base Metals in Manitoba. *Precambrian*, 1952, **25**, No. 4, 14 and 30.
16 Waldron, H. L. Sherritt Gordon Develops Lynn Lake Nickel-Copper. *Eng. and Min. J.*, 1951, **152**, 72-78.
17 Anon. Sherritt Gordon Mines, Ltd. Developments. *World Min.*, 1951, **4**, 54.
18 Anon. Sherritt Gordon Refinery. (Manitoba). *Canadian Min. J.*, 1952, February, 86.
19 Herneryd, O. Rationalisation of Copper Smelting and Electrothermic Lead Production at the Smelter at Ronnskär, Sweden, 1951. *Erzmetall*, 1951, **4**, November, 412-418. (In German).
20 Anon. Boliden Company's Expansion Programme. *Min. J.*, 1951, **237**, 478.
21 Bryk, P. Autogenous "Flash" Smelting of Copper Sulphide Concentrates. Reprint: Scand. Eng. Meeting, Helsinki, 1951, *J. Vuoriteollisuus.*
22 Goederitz, A. H. F. The Mansfield Copper-Bearing Shales and the Products Obtained from Them. *Metall u. Giessereitechnik*, 1951, **1**, No. 3, 71-76. (In German).
23 Prior, K. Seventy-five Years of Electrolytic Copper Refining at the Norddeutsche Affinerie, Hamburg. *Erzmetall*, 1951, **4**, No. 7, 245-249. (In German).
24 Anon. Yugoslavia Expanding Metal Production. *Min. J.*, 1952, **238**, February 22nd, 193.
25 Anon. New Mine in Yugoslavia. *Met. Ind.*, 1952, **81**, August 8th, 115.
26 Anon. Developing Copper in Israel. *The Times*, 1952, April 18th, 5.
27 Allgood, R. W. Sulphuric Acid and Liquid Sulphur Dioxide Manufactured from Smelter Gases at Copper Cliff, Ontario. *Canad. Min. Met. Trans.*, 1952, **55**, 123-125.
28 Oyama, T., and Tanaka, S. On the Emulsification of Flotation Reagents by Means of Ultrasonic Waves. *Sci. Rep. Res. Inst. Tohoku Univ.*, Series A, 1950, **2**, December, 925-927.
29 Schimmel, F. A. Electrolytic Refining of Copper from Ammoniacal Cuprous Salt Solutions. *Ind. Eng. Chem.*, 1951, **43**, December, 2943-2948.
30 Balint, I. Separation of Copper and Nickel. Hungarian Pat. No. 139,995.
31 Outokumpu, Oy, Bryk, P. B., and Aarnisalo, S. A. Direct Electrolytic Refining of Nickel from Nickel-containing Matte. Swed. Pat. No. 124,283.
32 Breton, E. J., and Schlechten, A. W. Separation of Copper from Zinc by Ion Exchange. *Trans. A.I.M.M.E.*, 1951, **191**, 517-521.
33 Trautzl, Peter, and Treadwell, W. D. Decomposition and Separation of Copper-Tin Alloys in a Stream of Hydrogen Chloride. *Z. f. Naturforschung*, 1951, **6b**, 229-232.
34 Anon. New Chemical Process Recovers Nickel, Cobalt, Copper Metal. *J. Metals.*, 1952, **4**, 589.
35 Thews, E. R. "Metallurgische Verarbeitung von Altmetallen und Ruckstanden." Band II, 1951. *Carl Hansen*, Munich, 290 pp.
36 Institute of British Foundrymen. Synthetic Resins in the Foundry. *Foundry Trade J.*, 1951, **91**, 3. *Amer. Foundryman*, 1952, **21**, February, 51.
37 Dews, J. W., and Drury, P. H. Synthetic Resins in the John Harper Foundry. *Foundry Trade J.*, 1952, **92**, May 22nd, 535.
38 Ames, B. N., Donner, S. B., and Kahn, N. A. Metallurgy of Shell Molding. *Amer. Foundryman*, 1952, **21**, January, 24.
39 Anon. Shell Mold Fog Lifting. *Amer. Foundryman*, 1952, **22**, July, 31.
40 Herold, R. Current Status of Shell Molding. *Amer. Foundryman*, 1952, **22**, August, 42.
41 Ames, B. N., Donner, S. B., and Kahn, N. A. The Shell Molding Process—Its Mechanics and Applications. *Foundry*, 1952, **80**, June, 112.
42 Cooper Alloy Foundry Co. Casting Stainless Steel in Shell Molds. *Foundry*, 1952, **80**, September, 108.
43 Sokolosky, W. A. Gating for Shell Molding. *Foundry*, 1952, **80**, August, 93.
44 Anglo-American Council on Productivity. The Brass Foundry. Report of Visit to U.S.A., 1950.
45 Anon. Shell Moulding Process. *Foundry Trade J.*, 1952, **93**, August 28th, 238.
46 Anon. In a Nutshell. *Foundry Trade J.*, 1952, **92**, June 12th, 613.
47 Hoff, O. Some recent Danish Experiments with the C-Process. Proceedings of the International Foundry Congress, Brussels, 1951, 399-408.
48 Polygram Casting Co., Ltd. Shell Moulding Process. Notes on the British Patent Position. *Foundry Trade J.*, 1952, **93**, November 20th, 582.
49 Mantle, E. C., and Potts, D. H. Aluminium Matchplate Patterns by the Pressure-cast Plaster Process. *Foundry Trade J.*, 1952, **93**, July 31st, 117, and August 7th, 157.
50 Anon. Beryllium Copper Cavities for Die Castings. *Precision Metal Molding*, 1952, **10**, August, 32-34.
51 Pfister, F. Statuary to Electronics via Plaster Moulding. *Foundry*, 1952, **80**, September, 86.
52 Skinner, R. A., and Ruddle, R. W. Insulating Feeders for Use with Copper-alloy Sand Castings. *Foundry Trade J.*, 1952, **93**, August 14th, 181.
53 Robinson, J. R. Knock-off Feeding Heads. *Foundry Trade J.*, 1952, **93**, July 3rd, 13.
54 Baker, W. A. Production of Serviceable Non-Ferrous Castings by Exploiting the Metal-Mould Reaction. Proceedings of the First World Metallurgical Congress, 1951, American Society for Metals.

55 Rutherford, N. B. The Effect of Mould Material and Alloying Elements on Metal-Mould Reaction in Copper-Base Alloys. *J. Inst. Metals*, 1951, **79**, 189.
56 Rutherford, N. B. The Effect of Metal-Mould Reaction on 88 : 5 : 5 : 5 Leaded Gunmetal Sand Castings. *J. Inst. Metals*, 1952, **80**, 555.
57 Mantle, E. C. Nitrogen Degassing and Metal Mould Reaction in the Production of Gunmetal Castings. *Foundry Trade J.*, 1952, **93**, July 24th, 95.
58 Baker, W. A. Phosphorus Deoxidation of Molten Copper. Proceedings of First World Metallurgical Congress, 1951, American Society for Metals, 268.
59 Swinyard, G. Grain Refinement of Non-Ferrous Castings. *Foundry Trade J.*, 1952, **92**, June 19th, 647.
60 Colton, R. A., and Margolis, M. Effects of Certain Elements on Grain Size of Cast Copper-Base Alloys. *Trans. Amer. Foundryman's Soc.*, 1951, **59**, 360.
61 Liddiard, P. D., and Forrester, P. G. Some Casting Problems of Copper-Lead Alloys. *Foundry Trade J.*, 1952, **92**, May 15th, 509.
62 Hargreaves, L. Production of Castings in Aluminium-Bronze, D.T.D.412. *Foundry Trade J.*, 1952, **92**, May 8th, 487.
63 Pierre, V. De., and Wynne, R. C. Production of Aluminium-Nickel Bronze Sand Castings. *Foundry*, 1952, **80**, July, 94.
64 Vanick, J. S. Nickel-Aluminium-Bronze. *Foundry*, 1951, **79**, September, 108–111.
65 Grand, L. Sand Cast Beryllium-Bronze. *Foundry Trade J.*, 1952, **93**, September 18th, 317.
66 Vanick, J. S. Cupro-Nickel Castings. *Foundry*, 1952, **80**, February, 100.
67 Hanson, D., and Pell-Walpole, W. T. Chill-Cast Tin Bronzes. First Ed., 1951, Arnold.
68 Voce, E. Cast Bronzes and Gunmetals. The Case for Fewer Specifications. *Tin and Its Uses*, 1952, May, 2.
69 Trigzs, W. W. Planetary Rolling Mill. Brit. Pat. No. 655,190.
70 Hessenberg, W. C. F., and Brit. I & S. Research Assoc. A New or Improved Method and Apparatus for Producing Sheet and Strip. Brit. Pat. No. 655,444.
71 Chappuis, J. A. A New or Improved Method and Apparatus for Shaping Metal Articles. Brit. Pat. 664,868.
72 Rolle, S. The Fabrication of Copper Wire. *Wire and Wire Prod.*, 1952, **27**, January, 35, 37–47, 76–83.
73 Blazey, C., and Benjamin, V. W. Some Principles of Continuous Wire Drawing. *Wire and Wire Prod.*, 1951, **26**, 751-757, 798.
74 MacLellan, G. D. S Some Friction Effects in Wire Drawing. *J. Inst. Metals*, 1952, **81**, September, 1.
75 Wistreich, J. G. The Wear of Wire Drawing Dies. *Nature*, 1952, **169**, March 15th, 450.
76 Ström, B. I., and Waller, B. G. The Cause of Check Marks on Copper Wire. Proceedings of the First World Metallurgical Congress, 1951, American Society for Metals, 338.
77 Ergang, R., and Weiz, S. Occurrence and Prevention of Flow Lines in Nickel Silver and Brass. *Z. Metallkunde*, 1952, **41**, February, 45–48.
78 Ergang, R. Stretcher Strains—Their Occurrence in Nickel Silver. *Met. Ind.*, 1952, **81**, October 3rd, 261.
79 Weber, R. D. The Cladding of Metals. *Metallurgia*, 1952, **45**, January, 3.
80 Anon. Royal Ordnance Factory, Radway Green, Crewe. *Engineer*, 1951, 191, June 1st, 732–733.
81 Reardon, E. J. Clad Steel Bullet Jackets Conserve Copper and Zinc. *Steel*, 1952, **130**, January 2nd, 68–69.
82 Tour, S. New Method Tested for Cladding Bullet Jackets. *Iron Age*, **169**, March 27th, 108–110.
83 Anon. Copper Cladding Process Shown. *Steel*, 1951, **129**, December 17th, 98.
84 Anon. New Copper Cladding Method to Help to Relieve Metal Shortage. *Electrical Engineering*, 1952, **71**, February, 197.
85 Anon. Applications of Copper-Clad Aluminium. *Metallurgia*, 1952, **46**, July, 39.
86 Knapp, A. P. How Lead-Clad Steel and Copper Extend Lead Applications. *Materials and Methods*, 1952, **36**, October, 115.
87 Brit. Non-Fer. Metals Res. Assn. Coating of Iron, Steel, Copper and Copper Alloy with Lead. Brit. Pat. 657,025, 1947, November 10th.
88 Canzler, H. Clad Steels and Their Application in Chemical Engineering. Preprint, 4th International Mechanical Engineering Congress, Stockholm, 1952, June.
89 Anon. New Use for Copper Cladding. *Steel*, 1952, **130**, May 26th, 120.
90 Anon. Stainless-Clad Copper Promises Improved High-Temperature Service. *Machine Design*, 1952, **24**, June, 141–142.
91 Kinney, J. Stainless-Clad Copper for High-Temperature Service. *Product Engg.*, 1952, **23**, April, 129–133.
92 Anon. Stronger, Lighter Jets from Clad Metals. *Steel*, 1952, **130**, May 19th, 104.
93 Davis, E., and Temple, S. G. Batch and Continuous Annealing of Copper and Copper Alloys. *J. Inst. Metals*, 1952, **80**, 287.
94 Evans, C. J., Hancock, P. F., Haywood, F. W., and McMullen, J. Electric Furnaces for the Thermal Treatment of Non-Ferrous Metals and Alloys. *J. Inst. Metals*, 1952, **80**, 255.
95 Waight, J. F. Gas Equipment for the Thermal Treatment of Non-Ferrous Metals and Alloys. *J. Inst. Metals*, 1952, **80**, 269.
96 Anon. Heat-Treatment Plant Developments. Recent Installations for Ferrous and Non-Ferrous Metals. *Metallurgia*, 1952, **45**, May, 231.
97 Jenkins, P. D. Recent Applications of High-Frequency Induction Heating in the Forging Industry. *Metallurgia*, 1952, **46**, September, 119.
98 Saltonstall, R. V. White Brass Plating. Paper read at 39th Annual Convention and 3rd Industrial Finishing Exposition of American Electroplaters Soc., 1952, June.
99 Anon. "White Brass" Undercoat may be the Answer to the Shortage of Nickel for Automobile Manufacturers. *Steel*, 1951, **129**, 57–58.
100 Schmerling, G. Modified Bronze Plating ("Nickelex"). *Met. Ind.*, 1952, **89**, 267.
101 Duc, F. S. Some Experience with a Proprietary Red Bronze Plating Solution as a Substitute for Nickel. *Electroplating*, 1952, **5**, April, 123.
102 Anon. Modern Finishes to Meet Present Supply Difficulties. *Prod. Finishing*, 1951, **4**, October, 51–55.
103 Anon. Alternative to Bright Nickel. *Electroplating*, 1952, **5**, May, 159.
104 Chadwick, S. The Direct Chromium Plating of Copper and its Alloys. I.M.F. Birmingham Autumn Conference. One-Day Conference for Practical Platers. *Bull. Inst. Met. Finishing*, 1952, **2**, Spring, 2–7.
105 Miller, W. G. Chromium on Copper and Its Alloys and Brass. I.M.F. Birmingham Autumn Conference. One-Day Conference for Practical Platers. *Bull. Inst. Met. Finishing*, 1952, **2**, Spring, 2–7.
106 Anon. Modern Finishes to Meet Present Supply Difficulties. *Prod. Finishing*, 1951, **4**, No. 9, 68–74.
107 Anon. Chromium Plating Without Nickel. *Machinery Lloyd*, 1951, 23, 95 : also *Electroplating*, 1951, **4**, 272.
108 Halls, E. E. Periodic Reverse Current Electroplating. *Prod. Finishing*, 1952, **5**, August, 61.
109 Jernstedt, G. W. P.R. Cyanide Copper Plating. Proceedings of the 36th Annual Convention of the American Electroplaters' Society, 1949, 68.
110 Jernstedt, G. W. Levelling with P.R. Current Plating. Proceedings of the 37th Annual Convention of the American Electroplaters' Society, 1950, 151.
111 Ruffle, T. W., and Chawner, P. M. H. "Migration" of Copper Plating in Box Carburising. *Metal Treatment*, 1952, **19**, June, 245.
112 Anon. Stopping-off Materials for Selective Nitriding. *Plating*, 1952, **39**, April, 387.
113 Anon. Textiles and Their Testing. H.M.S.O. (London), 1951, 41–44. (Based on R.A.E. Report: Metal-plated Fabric Substitute for Wire Gauze: Laboratory Tests for Durability. By F. Millard and E. Whatham).
114 Anon. Textiles and Their Testing. H.M.S.O. (London), 1951., 45–50. (Based on R.A.E. Report: Further Laboratory Durability Tests on Metal-plated Fabric as a Substitute for Wire Gauze. By F. Millard).
115. Edwards, J. An Experimental Study of Electropolishing. *J. Electrodepositors Tech. Soc.*, 1952, **28**.
116 Munse, W. H., and Weil, N. A. Mechanical Properties of Copper at Various Temperatures. *Proc. A.S.T.M.*, 1951, **51**, 996–1022.
117 Russell, A. S. Effect of Heating at 300° and 500° F. on the Properties of Aluminium and Copper Wire. *Wire and Wire Products*, 1952, **27**, March, 255–256.
118 Westbrook, J. H. Temperature Dependence of Hardness of Pure Metals. 1952, American Society of Metals, Preprint No. 17.
119 Cook, M., Fentiman, W. P., and Davis, E. Observations on the Structure and Properties of Wrought Copper-Aluminium-Nickel-Iron Alloys. *J. Inst. Metals*, 1952, **80**, April, 419.
120 Kasberg, A. H., and Muck, D. J. Isothermal Transformation and Properties of a Commercial Aluminium Bronze. *J. Metals*, 1951, **3**, October, 903–908.
121 Carter, J. J., Mends, D. M., and McKeown, J. The Creep and Fatigue Properties of Two Commercial Aluminium Bronzes at 500° C. *Metallurgia*, 1952, **45**, June, 273.
122 Sopwith, D. G. The Resistance of Aluminium and Beryllium Bronzes to Fatigue and Corrosion Fatigue. 1951, Aeronautical Research Council. R. & M. No. 2486, 1951.
123 Gough, H. J., and Sopwith, D. G. The Resistance of Some Special Bronzes to Fatigue and Corrosion-Fatigue. *J. Inst. Metals*, 1937, **60**, 143.
124 Moyle, V. A. B., and Moyle, C. E. Improvements in or Relating to Copper-Containing Alloys. Brit. Pat. No. 654,970.
125 Richards, J. T. A Review of Beryllium and Beryllium Alloys. *J. Metals*, 1951, **3**, 379–386.
126 Richards, J. T., Levan, R. K., and Smith, E. M. The Influence of Cold Work and Heat Treatment on the Engineering Properties of Beryllium Copper Wire. *Proc. A.S.T.M.*, 1951, **51**, 771–791.
127 Richards, J. T. Beryllium Copper Wire: Part I.—Its Processing and Uses. Part II.—Property and Design Considerations. *Wire and Wire Prod.*, 1952, **27**, February, 149–154, 192–193, 195, March, 257–262, 303–307.
128 Richards, J. T., and Smith, E. M. Forming Characteristics of Beryllium Copper Strip. *Proc. A.S.T.M.*, 1950, **50**, 1085–1099.
129 Geisler, A. H., Mallery, J. H., and Steigert, F. E. On the Mechanism of Precipitation in Copper-Beryllium Alloys. *J. Metals*, 1952, **4**, March, 307.
130 Grubl, W., and Wassermann, G. Segregation Process in Copper-Beryllium Alloys. *Metall*, 1951, **5**, March, 93–98, April, 141–145. (In German).
131 Bailey, G. L. Copper-Nickel-Iron Alloys Resistant to Sea-Water. *J. Inst. Metals*, 1951, **79**, July, 243.
132 Palmer, E. W., and Wilson, F. H. Constitution and Properties of Some Iron-Bearing Cupro-Nickels. *J. Metals*, 1952, January, 55–64.
133 Meikk-Oja, H. M. Segregation of Iron and Phosphorus at the Grain Boundaries in 70 : 30 Brass During Grain Growth. *J. Inst. Metals*, 1952, **80**, June, 569.
134 Sinclair, G. M., and Craig, W. J. Influence of Grain Size on Work Hardening and Fatigue Characteristics of Alpha Brass. *Trans. Amer. Soc. Met.*, 1952, **44**, 929–948.
135 Morris, A. Production of Age-Hardened Copper Base Alloy Products Canadian Pat. No. 478,288.
136 Morris, A. Hardenable Copper-Base Alloys and Fabrication Thereof. Canadian Pat. No. 478,289.
137 Morris, A., and Blomquist, H. V. Hardenable Copper-Base Alloys and Their Fabrication. Canadian Pat. No. 478,290.
138 Chase Brass and Copper Co. Inc. Age-Hardened Copper-Base Alloy. Brit. Pat. No. 655,628.
139 Karlsson, N. An X-ray Study of the Phases in the Copper-Titanium System. *J. Inst. Metals*, 1951, **79**, 391–405.
140 Joukainen, A., Grant, N. J., and Floe, C. F. Titanium-Copper Binary Phase Diagram. *J. Metals*, 1952, **4**, July, 766.
141 Betterton, J. O., and Hume-Rothery, W. The Equilibrium Diagram of the System Copper-Gallium in the Region 30–100 at. % Gallium. *J. Inst. Metals*, 1952, **80**, April, 459.
142 Reynolds, J., Wiseman, W. A., and Hume-Rothery, W. The Equilibrium Diagram of the System Copper-Indium in the Region 25-35 at. % Indium. *J. Inst. Metals*, 1952, **80**, August, 637.
143 Basinski, Z. S., and Christian, J. W. The Cubic-Tetragonal Transformation in Manganese-Copper Alloys. *J. Inst. Metals*, 1952, **80**, August, 659.
144 Greenfield, P., and Raynor, G. V. The Constitution of the Copper-Rich Copper-Zinc-Germanium Alloys. *J. Inst. Metals*, 1952, **80**, March, 375.
145 Klepps, O. J., and Weil, J. A. The Solubility of Copper in Liquid Lead Below 950°. *J. Am. Chem. Soc.*, 1951, **73**, 4848–4850.
146 Kamibayashi, K. Alloy Containing a Small Amount of Zirconium. Japanese Pat. No. 176,653.
147 Gebhardt, E., and Dreher, M. On Constitution of Copper-Silver-Indium System I. Equilibrium Process on the Copper-Silver Side. *Metallkunde*, 1951, **42**, 230–238.
148 Koster, W. Ternary System Copper-Nickel-Magnesium. *Metallkunde*, 1951, **42**, 326–327.
149 Allen, N. P., Schofield, T. H., and Tate, A. E. L. Mechanical Properties of α-Solid Solutions of Copper with Zinc, Gallium, Germanium and Arsenic. *Nature*, 1951, **168**, September 1st, 378.
150 Hargreaves, M. E. Modulated Structures in Some Copper-Nickel-Iron Alloys. *Acta. Cryst.*, 1951, **4**, 301–309.
151 Stewart, W. C., and La Que, F. L. Corrosion Resisting Characteristics of Iron Modified 90 : 10 Cupro Nickel Alloy. *Corrosion*, 1952, **8**, August, 259–277.
152 Risbridger, C. A. Effect of Chlorination of Drinking Water on Brass Fittings. *J. Inst. Water Eng.*, 1952, **6**, February, 65–73.
153 Ingleson, H., Sage, A. M., and Wilkinson, R. Effect of Chlorination of Drinking Water on Brass Fittings. *J. Inst. Water Eng.*, 1949, **3**, 81.
154 Bulow, C. L. Dezincification of Aluminium Brass Condenser Tubes Prevented by Chlorination and Cleaning. *Corrosion* (*News Section*), 1951, **7**, July, 1.
155 Clenny, J. T. Stress Corrosion of Cast Bronzes Evaluated. *Iron Age*, 1951, **367**, June 21st, 85–89.
156 Silk, E. J. Nylon: A Factor in Stress Corrosion of Aluminium Bronze. *J. Metals*, 1951, **3**, 600.
157 Kaneda, Y. Season Cracking of Manganese Brass Propellers. Proceedings of the First World Metallurgical Congress, 1951, American Society for Metals, 637.

158 Lessner, O. Stress-Corrosion in Special Copper Alloys. Preprint of paper read at 4th International Mechanical Engineering Congress, Stockholm, 1952, June.
159 Bulow, C. L. Comparative Tests on Admiralty Brass and other Brasses After Immersion in Sodium Bichromate Solution Containing Some Sulphuric Acid Solution. *Corrosion*, 1951, **7**, No. 6, 20.
160 Morton, B. B. Selecting Alloys to Resist Corrosion in Oil Refineries. *Petroleum Processing*, 1951, **6**, No. 11, 1233–1235.
161 Bukowiecki, A. Corrosive Effects of Motor Gear Oils. *Schweiz. Arch. angew. Wiss. Techn.*, 1951, **17**, No. 6, 182–191. (In German).
162 Sawyer, D. W. Catalytic Effect of Several Metals on the Oxidation of Lubricating Oils. *Mech. Eng.*, 1951, **73**, August, 666.
163 Barnes, H. Studies on Antifouling Compositions. VII. Leaching Rate During the Middle and Late Stages of Compositions Based on Cuprous Oxide as the Toxic Component. *J. Iron and Steel Inst.*, 1951, **169**, 360–367.
164 Stroud, E. G., and Vernon, W. H. J. Prevention of Corrosion in Packaging. I.—Use of Sodium Benzoate as a Corrosion-Inhibitor in Wrappings. *J. Appl. Chem.*, 1952, **11**, April, 166–172.
165 Gas Research Board. The Resistance to Corrosion of Materials of Construction. (Solder Coatings on Copper in Gas Appliances). Gas Research Board: Report of the Director for the Year 1950, 1951 (Publn. CRB 60), 49–52.
166 Parker, C. D. Bacterial Corrosion of Construction Material. *Commonwealth Eng.*, 1951, **39**, December 1st, 190–196.
167 Mosboro, R. J., Bohl, R. W., Howland, F. L., and Nunse, W. H. Tensile Tests and Metallurgical Studies of Welded Copper Joints. *Welding Jnl.*, 1951, October, 519s–528s.
168 Galton, F. T. The Welding of Copper Pressure Vessels by Means of the Oxygen Acetylene Process. *Australasian Engineer*, 1951, October 8th, 70–73.
169 Shashkov, A. N., and Khromov, Z. S. Nitrogen Arc Welding of Copper. *Avtogennoe Delo.*, 1951, No. 9, 4–7.
170 Anon. Copper-Brazing Stainless Steel Without Flux. *Steel*, 1952, January 14th.
171 Hofmann, W., Husman, H. J., and Koppe, R. Pressure Welding of Aluminium to Copper as Autogenous Soldering. Paper presented at the General Meeting of the Deutsche Gesellschaft fur Metallkunde, Berlin, 1951, September 8th.
172 Bailey, G. L. J., and Watkins, H. C. The Flow of Liquid Metals on Solid Metal Surfaces and its Relation to Soldering, Brazing, and Hot-Dip Coating. *J. Inst. Metals*, 1951, **80**, October, 57.
173 Cabarat, R., Gence, P., Guiliet, L., and Le Roux, R. Thermoelastic Analysis of Transformations in Copper Alloys. *J. Inst. Metals*, 1951, **80**, December, 151.
174 Beck, L. H., and Smith, C. S. Copper-Zinc Constitution Diagram, Redetermined in the Vicinity of the Beta Phase by Means of Quantitative Metallography. *J. Metals*, 1952, **4**, October, 1079.
175 Rhines, F. N., and Newkirk, J. B. The Order-Disorder Transformation Viewed as a Classical Phase Change. 1952, American Society for Metals, Preprint No. 12.
176 Channon, S. L., and Walker, H. L. Recrystallisation and Grain Growth of Alpha Brass. American Society for Metals, 1952, Preprint No. 8.
177 Chiche, P., and Dode, M. Standard Thermodynamic Properties of Copper Oxides. *Comptes Rendus*, 1951, **232**, No. 7, 618–620. (In French).
178 Lumsden, J. Thermodynamics of Alloys. Inst. Met. Monograph and Report Series, No. 11, 1952, 390 pp.
179 Ellwood, E. C., and Weddle, W. A. The Production and Properties of Oxide-Reduced Copper Powder. *J. Inst. Metals*, 1952, **80**, January, 193.
180 Butler, J. M., and Hoar, T. P. Unrelated Simultaneous Interdiffusion and Sintering in Copper-Nickel Compacts. *J. Inst. Metals*, 1952, **80**, January, 207.
181 Howat, D. D., Craik, R. L., and Cranston, J. P. The Sintering of Copper-Zinc Powder Compacts. *J. Inst. Metals*, 1952, **80**, March, 353.
182 Dale, J. Powder Metallurgy Produces a Brass Ordnance Component; The Full Case History of an Important Piece. *Precision Metal Molding*, 1952, **10**, February, 34–36, 69–72.
183 Anon. Powdered Metals May Answer High Temperature Problem. *Prod. Eng.*, 1951, **22**, May, 123.
184 Goetzel, C. G. Infiltration Metallurgy. *Research*, 1951, **4**, 555–561.
185 Lenel, F. V. Sintering with a Liquid Phase, "The Physics of Powder Metallurgy: A Symposium," 1951, McGraw-Hill, 238–255.
186 Stern, G. Investigation of the Effect of Final Density of Copper Infiltrated Iron on Physical Properties. *Powder Met. Bull.*, 1951, **6**, April, 57–62.
187 National Lead Co. Metallic Composition Adapted for Use as a Bearing Metal. Brit. Pat. No. 658,907.
188 Glacier Metal Co., Ltd., and Tait, W. H. Plain Bearings or the Like. Brit. Pat. No. 657,080.
189 Glacier Metal Co., Ltd. Plain Bearings or the Like. Brit. Pat. No. 657,085.
190 Naeser, C. Rolling of Metal Powders. Preprint of Paper read at 4th International Mechanical Engineering Congress, Stockholm, 1952, June, 14 pp.
191 Primavesi, D. Process for the Electrolytic Production of Copper in Powder Form. Brit. Pat. No. 668,470.
192 Langford, K. E. Analysis of Electroplating and Related Solutions. 1951, Electroplating and Metal Finishing, 400 pp.
193 Twyman, F. Metal Spectroscopy, 1951, Griffin, 569 pp.
194 Schatz, F. V. The Spectrochemical Determination of Zinc, Lead, and Iron in Copper and Copper Alloys. *J. Inst. Metals*, 1951, **80**, October, 77.
195 Hans, A. Direct Spectrographic Analysis of Brasses. Groupe pour l'Avancement des Méthodes d'Analyse Spectrographique des Produits Metallurgiques, 13th Congress, June, 1950, 75–79. (In French).
196 Murdza, N. H. Effect of Speed of Testing on the Tensile Properties of Copper and Copper-Base Alloys. American Society for Testing Materials, 1952, Preprint No. 11a.
197 Marshall, E. R., and Shaw, M. C. The Determination of Flow Stress from a Tensile Specimen. *Trans. Amer. Soc. Met.*, 1952, **44**, 705–725.
198 Simmons, A. L. Hot Forging Tests on Some Copper-Base Alloys. *Australian J. Appl. Sci.*, 1951, **2**, March, 76–88.
199 Roberts, I. Prediction of Relaxation of Metals from Creep Data. American Society for Testing Materials, 1951, Preprint No. 37, 15 pp.
200 Teed, P. L. Stratospheric Flight and Metallurgy. *Aeroplane*, 1952, **82**, March 21st, 334–335.
201 Braidwood, R. J., Burke, J. E., and Nachtrieb, N. H. Ancient Syrian Coppers and Bronzes. *J. of Chemical Education*, 1951, **28**, February, 87–96.
202 Root, W. C. Gold-Copper Alloys in Ancient America. *J. of Chemical Education*, 1951, **28**, February, 76–78.
203 Hunt, L. B. Electrical Contacts; A Book of Reference for the Electrical Engineer. London, 1946, Matthey, 122 pp.
204 Street, A., and Alexander, W. Metals in the Service of Man, Rev. Ed., 1951, Penguin, 237 pp.
205 Freeman, J. R. Copper an Example of Old Material with New Possibilities. *Amer. Soc. Met.* (Montreal), March, 1951.

New Equipment to Speed Aircraft Production at Short Brothers

A HUFFORD stretch-wrap forming machine has recently been delivered to the Newtownards Factory of Short Bros. and Harland Ltd. First of its kind in Northern Ireland, the machine, which is valued at £100,000, will be used to step-up production of air frame parts for aircraft being manufactured at Belfast. Short Bros. are already producing the Canberra high-speed twin-jet bomber and will be starting manufacture of Comets in the near future.



The Hufford machine weighs almost 75 tons and special arrangements were made for its transportation from Belfast Docks to the factory. It has a 150-ton pull and can accommodate skin sheets up to 66 in. long and $\frac{3}{32}$ in. thick, and dies up to 76 in. for 180° bend at full tonnage. With this simple and fast process, parts that would otherwise be difficult to form can be set up for normal production runs.

In the Hufford system, a die possessing the desired contour is securely mounted and remains immovable during the forming process. The work is held in tangency to the front of the die and stretched almost to yield point. With tension maintained, the work is wrapped around the die, accurately moulding itself into and around each die configuration. Upon completion of the wrap, another stretch is applied which strength exceeds the elastic limit of the workpiece. This second stretch "sets" the contour shape and simultaneously raises the yield strength of the material. Upon release, the part retains the shape imparted by the die curves.

Behaviour of Carbides in Niobium Stabilised Austenitic Stainless Steel*

By T. V. Simpkinson†

It is shown that in properly processed niobium stabilised 18–8 *the carbon is immobilised as a difficultly soluble random precipitate of niobium carbide. How variations in the temperature of final hot working, in heat treatment, and in welding, affect the type and distribution of precipitated carbides seen under the microscope is discussed and illustrated. Improper processing may leave* 18–8*Nb in a condition of susceptibility to intergranular corrosion.*

AN inherent shortcoming that may seriously impair the serviceability of 18%Cr–8%Ni stainless steel is a susceptibility to intergranular corrosion which results from heating within a "sensitisation" temperature range, as unavoidably occurs during welding or during service at critical temperatures. A condition that accompanies this sensitisation is a precipitation, at the austenite grain boundaries, of a carbide rich in chromium. Such precipitation may occur within the general temperature range of 750° to 1,650° F. (400° to 900° C.), but susceptibility to intergranular corrosion most readily develops within the more restricted range of about 850° to 1,475° F. (455° to 800° C.).

This shortcoming may be remedied by the addition, in sufficient amount, of strong carbide-forming elements such as niobium and titanium. When either of these elements is present, and after proper processing, the carbon is immobilised as a difficultly soluble dispersed precipitate of niobium or titanium carbide‡; thus, the formation of chromium-rich grain boundary carbide is avoided.

The present paper is concerned only with the niobium "stabilised" 18–8 stainless steel designated by the American Iron and Steel Institute as Type 347. The paper is restricted to the study of the "carbide" phase, describing how it occurs in the steel "as cast" and how variations in the temperature of final hot working, in heat treatment, and in welding, affect the type and distribution of precipitated carbides.

The analyses of the steels studied microscopically are given in Table I.

TABLE I.—IDENTIFICATION AND ANALYSIS OF STEELS.

Steel	C%	Mn%	Si%	Cr%	Ni%	Nb%	Ratio Nb/C	Photomicrographs
A	0·10*	0·38	0·45	17·6	11·3	0·76	7·6	1, 2, 7, 8, 9, 10
B	0·08	1·54	0·80	17·9	10·4	0·91	11·4	3
C	0·06	1·60	0·52	18·6	11·1	0·81	13·5	6, 11, 12, 13, 14, 15, 16, 17, 18
D	0·10	0·51	0·59	18·0	10·0	0·83	8·3	5

* Above standard specified maximum.

The etching reagent employed was a 10% aqueous solution of sodium cyanide used electrolytically at six volts.

Eutectic "Carbide"

Under the microscope, 18–8Nb stainless steels are readily distinguishable from straight 18–8, since "as polished" they show relatively large characteristic "inclusions." This phase has been identified by Dulis and Smith as essentially a solid solution of NbC and

* Published by permission of the Director-General of Scientific Services, Department of Mines and Technical Surveys, Ottawa, Canada.

† Physical Metallurgist, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa.

‡ The "carbides" are in all probability basically solid solutions of NbC–NbN and TiC–TiN, respectively. See reference (1).

1 "Identification of Inclusions in Austenitic 18Cr–8Ni–Cb (Type 347) Steel," by E. J. Dulis and G. V. Smith. *Transactions, American Society for Metals*, **44**, 1952, 877 to 881.

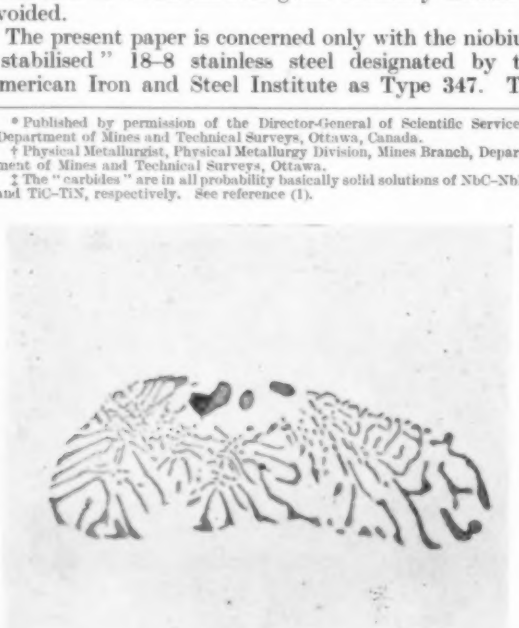


Fig. 1.—30 lb. casting: eutectic carbide in austenite matrix. Electrolytically etched in 10% NaCN for 15 seconds. × 1,500

Fig. 2.—30 lb. casting: eutectic carbide is at grain boundary and within grains. Electrolytically etched in 10% NaCN for 15 seconds. × 250

All photomicrographs enlarged 10% linear in reproduction.

Fig. 3.—Hot-rolled ¾ in. bar : eutectic carbide in stringers. Unetched. × 250

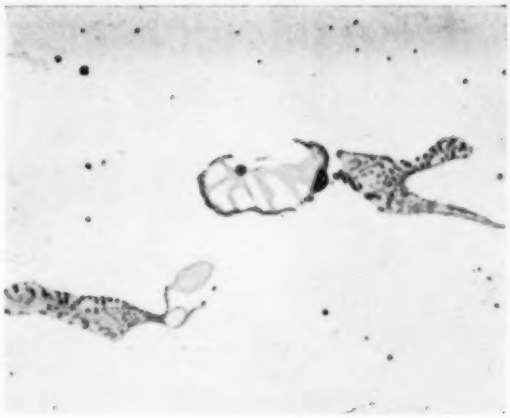


Fig. 4.—Weld metal : eutectic carbide and ferrite in austenite matrix. Electrolytically etched in 10% NaCN for 30 seconds. × 1,500

NbN with approximately equal amounts of carbon and nitrogen. An examination of Type 347 castings reveals that this phase occurs as a eutectic constituent, located at the boundaries of the austenite crystals and also within the crystals in an interdentritic pattern. The phase is illustrated at high magnification in Fig. 1, while Figs. 2 and 10, at lower magnification, show the distribution of the eutectic groups. In the following discussion this phase will be referred to as eutectic carbide. The specimens of Figs. 1 and 2, taken from a 30-lb. sand casting (Steel A in Table I), were electrolytically etched for fifteen seconds in sodium cyanide to improve contrast for photographic purposes, but all the eutectic carbide was visible "as polished." Fig. 3, unetched, is of a ¾-in. section hot rolled from a 16-in. ingot (Steel B). This carbide is not dissolved to any extent at normal hot rolling temperatures, hence the colonies formed in the ingot are simply rolled out into elongated groups in the austenite matrix.

Fig. 4 illustrates some features of the microstructure of 18–8Nb weld metal "as welded," deposited by the argon arc method. The constituent in a eutectic pattern, just discernible in this micrograph, is undoubtedly identical with that shown in Figs. 1 and 2. The same constituent is found in Type 347 parent metal immediately adjoining welds and at the edge of flame-cut plates. An area in the parent metal next the weld shown in Fig. 4, is illustrated in Fig. 5.

The effect of very high reheating temperatures upon the eutectic carbide in samples of rolled ¼-in. plate (Steel C) was studied. With holding times of one hour, temperatures up to 2,300° F. (1,260° C.) had no visible effect, but some solution of this phase occurred at 2,350° F. (1,285° C.). After two hours at 2,500° F. (1,370° C.) solution had taken place to a considerable degree, and after four hours at this temperature all elongated groups of eutectic carbide had completely disappeared. However, this phase was now present at grain boundaries and within the grains in a distinct eutectic pattern. Evidently incipient melting had occurred, with the result that eutectic carbide formation took place when the specimen was quenched; this formation is illustrated in Fig. 6. (See also Figs. 15 and 16.)

Heating samples from the casting illustrated in Figs. 1 and 2 (Steel A), for four hours at 2,500° F. (1,370° C.)

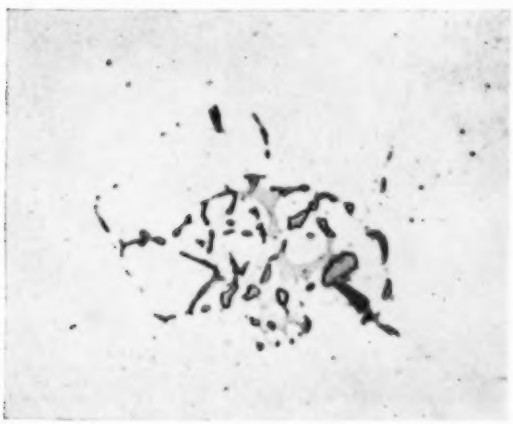


Fig. 5.—Parent metal very near weld : eutectic carbide and ferrite (faint) in austenite matrix. Electrolytically etched in 10% NaCN for 30 seconds. × 1,500

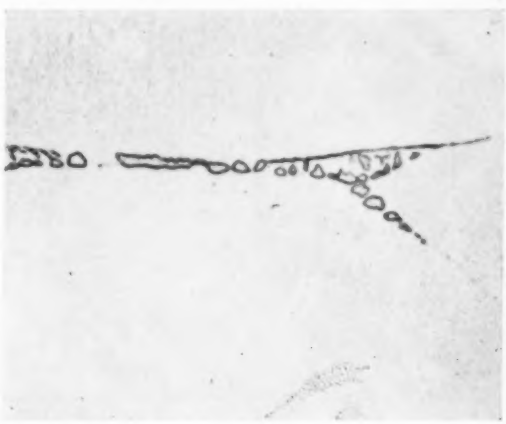


Fig. 6.—Plate heated to 2,500° F. (1,370° C.) : eutectic carbide in austenite matrix. Electrolytically etched in 10% NaCN for 30 seconds. × 1,500

Fig. 7.—Casting in the "as cast" condition: eutectic carbide and cloud of dot carbides. Electrolytically etched in 10% NaCN for 2–3 minutes. × 1,500

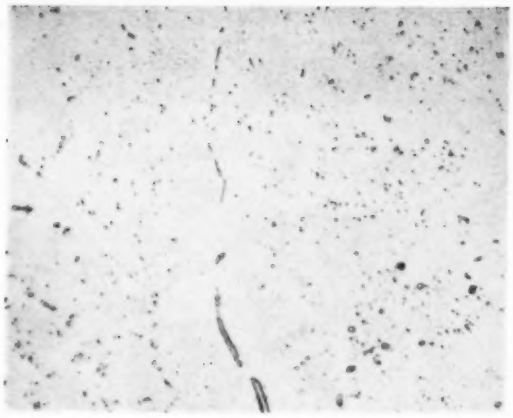


Fig. 8.—Casting, quench annealed at 2,000° F. (1,095° C.): dot carbide more dispersed. Electrolytically etched in 10% NaCN for 2–3 minutes. × 1,500

modified the shape and distribution of the eutectic carbide but the amount present remained nearly the same.

Holzworth, Beck and Fontana[2] observed a "dark grain boundary zone" in samples of $\frac{1}{16}$-in. plate of Type 347 that had been water quenched after heating half hour at 2,500° F. (1,370° C.). Doubtless what they observed was the phase illustrated by Fig. 6 of the present paper.

Dispersed "Dot Carbide"

In addition to eutectic carbide, 18–8Nb steels contain a large amount of carbides that precipitate after the completion of solidification, as the casting cools initially and during subsequent reheatings. Unlike the eutectic carbide these latter are visible only after suitable etching. These "dot carbides" are normally of a particle size too small to be resolved into circles by the light microscope. In suitably etched microspecimens viewed under reflected white light their presence is indicated by innumerable black dots, and when dark-field illumination is used they appear as bright points of light. The microstructure, revealed by etching two to three minutes in 10% sodium cyanide, of the cast material shown lightly etched in Figs. 1 and 2, is illustrated in Figs. 7 to 10 inclusive. The carbon content of this particular cast of steel is above the standard specified maximum of 0·08%, and the ratio of niobium to carbon is low. However, it is believed that this deviation from the standard composition will have caused no essential departure from normal in the microstructures developed. Figs. 7 and 9 are of the material "as cast," while Figs. 8 and 10 are of a specimen water-quenched after heating for two hours at 2,000° F. (1,095° C.). In the "as cast" steel, the dot carbides are heavily concentrated in clouds, these cloud concentrations occurring in a pattern that reveals the dendritic nature of the steel (Fig. 9). They are seen to be preferentially located between the ribs of the austenite dendrites with the dendrite ribs themselves being poor in precipitated carbides.

Heat treatment at 2,000° F. (1,095° C.) has caused partial solution of the dot carbides in the cloud concentrations and precipitation of carbide in carbide-poor areas, thus greatly reducing the unevenness of distribution of the fine precipitates (see Fig. 10). Because

2 "The Mechanism of Knife-Line Attack in Welded Type 347 Stainless Steel," by M. L. Holzworth, F. H. Beck and M. G. Fontana. *Corrosion*, **7**, December, 1951, 441 to 449.

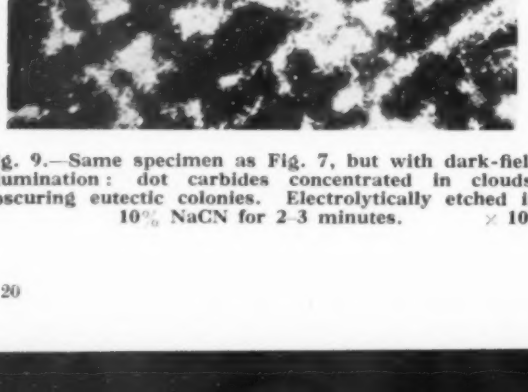


Fig. 9.—Same specimen as Fig. 7, but with dark-field illumination: dot carbides concentrated in clouds, obscuring eutectic colonies. Electrolytically etched in 10% NaCN for 2–3 minutes. × 100

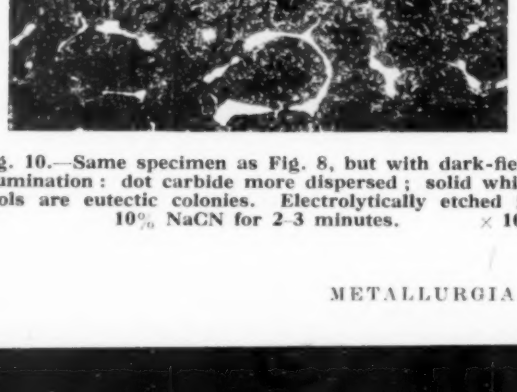


Fig. 10.—Same specimen as Fig. 8, but with dark-field illumination: dot carbide more dispersed; solid white pools are eutectic colonies. Electrolytically etched in 10% NaCN for 2–3 minutes. × 100

Fig. 11.—Plate, quench-annealed 1,950° F. (1,065° C.): heavy random precipitation of dot carbide in austenite matrix; there is some eutectic carbide. Electrolytically etched in 10% NaCN for 5 minutes. × 500

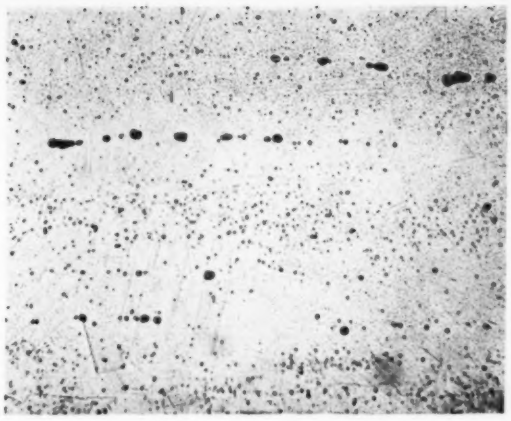


Fig. 12.—Plate, quench-annealed 2,150° F. (1,175° C.): dot carbide partially dissolved. Electrolytically etched in 10% NaCN for 5 minutes. × 500

both solution and precipitation of carbide has occurred simultaneously while the cast specimen was held at 2,000° F. (1,095° C.), there must be at least two kinds of dot carbides* in the "as cast" structure, one kind having considerable solubility at 2,000° F. (1,095° C.) and another kind having little solubility at this temperature. As stated in the introduction, when straight 18–8 steels are heated in, or slowly cooled through, the general temperature range of 750°–1,650° F. (400°–900° C.), carbide rich in chromium precipitates. This carbide can be completely redissolved by reheating in the approximate range of 1,800°–2,000° F. (980°–1,095° C.). The dot carbide in 18–8Nb that is relatively insoluble at 2,000° F. (1,095° C.) is believed to be niobium "carbide" containing negligible chromium†, and it seems logical to conclude that the carbide that dissolved at 2,000° F. (1,095° C.) is chromium-rich carbide which had precipitated in the cloud concentrations as the casting slowly cooled through temperatures somewhere below 1,650° F. (900° C.). It should be mentioned that the grain boundaries "as cast" were occupied by dot carbide as well as by eutectic carbide. The former was almost completely dissolved by the 2,000° F. (1,095° C.) treatment and, therefore, is also believed to be chromium-rich carbide. It is reasonable to expect that a considerable amount of niobium carbide precipitated as the casting cooled initially, and certainly heating at 2,000° F. (1,095° C.) caused further precipitation of this phase, largely in the carbide-poor ribs of the dendrites. The rate of initial cooling of the casting was probably sufficiently rapid to hold niobium carbide in solution well beyond the equilibrium amount, with the result that precipitation of this carbide would occur during reheating at 2,000° F. (1,095° C.); furthermore, as soon as chromium carbide was dissolved at this temperature the carbon contained therein would tend to combine with excess niobium and be reprecipitated as niobium carbide.

In wrought steels, precipitation of carbon as niobium carbide is substantially completed during the process of heating and hot working, when this is carried out at temperatures that are not too high, so that the carbon is effectively tied up as a random precipitate before the steel has cooled to the temperature range in which chromium-rich carbide may form. The formation of chromium carbide is now prevented during subsequent reheating so long as reheating temperatures are below that necessary to dissolved niobium carbide. Consequently, even prolonged heating in the range that causes sensitisation to intergranular corrosion in straight 18–8 does not have this effect on properly processed 18–8Nb of sufficient niobium content, and no precipitation of carbide at grain boundaries occurs.

The structure of an 18–8Nb ¼-in. plate (Steel C) rolled in the normal manner and quench annealed from 1,950° F. (1,065° C.) is shown in Fig. 11. The dot carbide which was undoubtedly segregated in the cast ingot, is seen to have been more or less randomly dispersed by the combined effects of heating and working, while the eutectic clusters are seen as elongated groups. A smaller amount of eutectic carbide is present than in the steel of Fig. 3.

Specimens of the ¼-in. Steel C plate were quench-annealed at successively higher temperatures, using 50° increments, from 1,900° to 2,300° F. (1,035° to 1,260° C.). The holding time at each temperature was one hour. With temperatures up to 2,050° F. (1,120° C.), microexamination failed to indicate any appreciable solution of dot carbide, Fig. 11 being typical of all specimens heated at 1,900° to 2,050° F. (1,035° to 1,120° C.). Fig. 12 shows the structure of a specimen quench-annealed at 2,150° F. (1,175° C.). Partial solution of the carbide has taken place and evidence of persistent dot carbide segregation is revealed. Solution of the dispersed dot carbides was complete at 2,300° F. (1,260° C.).

In practice, annealing temperatures above 2,050° F. (1,120° C.) are generally not resorted to, as the purpose of annealing is not to dissolve niobium carbide but rather to dissolve any chromium-rich carbide that may be present, or to soften the steel and reduce residual stresses. Temperatures as low as 1,700° F. (925° C.) are sometimes used. In special cases where attainment of maximum softness is of importance, temperatures somewhat higher than 2,050° F. (1,120° C.) may be required. Several investigators have shown that increasing the annealing temperature of Type 347 steel tends to cause

* When the dot-like precipitate is believed to be all of one kind the singular, "carbide," is used in referring to it and when two kinds are believed to be present the plural, "carbides," is used.

† Like the "eutectic carbide," the "dot carbide" is in all probability basically a solid solution of NbC and NbN[1].

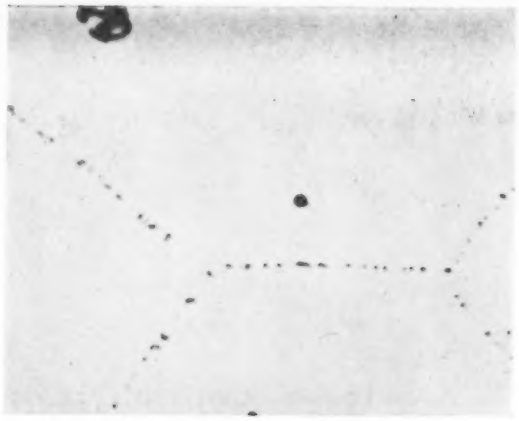


Fig. 13.—Plate, quench-annealed 2,400° F. (1,315° C.): grain boundary precipitation. Electrolytically etched in 10% NaCN for 30 seconds. × 1,000

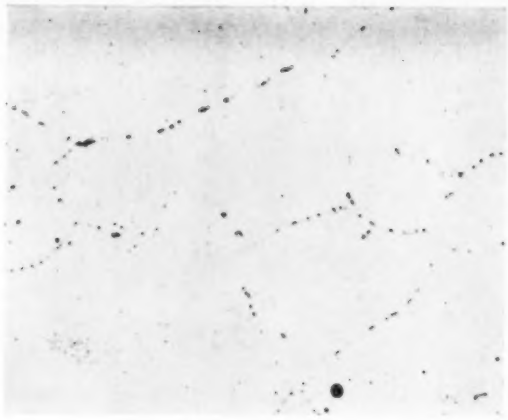


Fig. 14.—Near flame-cut edge of ¼ in. plate: grain boundary precipitation. Electrolytically etched in 10% NaCN for 5 minutes. × 500

increased susceptibility to intergranular corrosion after subsequent reheating in the sensitisation temperature range. For this reason, it is generally recommended that annealing be done at the lowest temperature feasible. Apparently there is some solution of niobium carbide with annealing temperatures even lower than 2,050° F. (1,120° C.) and if reheating in the sensitisation range occurs, some degree of harmful chromium-rich carbide precipitation takes place.

Grain Boundary Precipitation

(*a*) *Developed Near* 2,400° *F.* (1,315° *C.*).

When samples of Plate C were heated at temperatures between 2,300° and 2,500° F. (1,260° and 1,370° C.) followed by water quenching, a grain boundary precipitate appeared, the precipitation being heavier the higher the temperature of reheating. This constituent was visible only after suitable etching. Fig. 13 shows the microstructure found in a sample held for half an hour at 2,400° F. (1,315° C.) and water quenched. The behaviour among different Type 347 samples was variable as regards the amount of such high temperature precipitation. Some samples showed it only when heated above about 2,400° F. (1,315° C.). A similar precipitate, illustrated in Fig. 14, was found immediately adjacent to the melted zone at the flame-cut edge of a ¼-in. Type 347 plate and one would expect that under some conditions of welding such precipitation would occur in Type 347 parent metal. The flame-cut plate in question was air cooled after cutting but it is believed that the precipitation occurred while the zone in question was at the very high temperature reached during cutting, and not subsequently as the plate cooled. Fig. 15 is of the same sample as Fig. 6 (Type 347 plate held at 2,500° F. (1,370° C.) four hours.) In this micrograph a constituent having a distinct eutectic pattern is associated with a row of particles precipitated along a grain boundary. Another area of the same sample is shown in Fig. 16. At lower magnification (not shown), the grain boundaries of this specimen were seen to be almost completely outlined by such rows of particles along with eutectic groups. One would suspect that the fine grain boundary precipitate under discussion and the eutectic constituent are the same phase, namely, NbC–NbN solid solution.

In the paper[2] previously referred to, Holzworth, *et al* include a micrograph at ×500 of Type 347 heated for

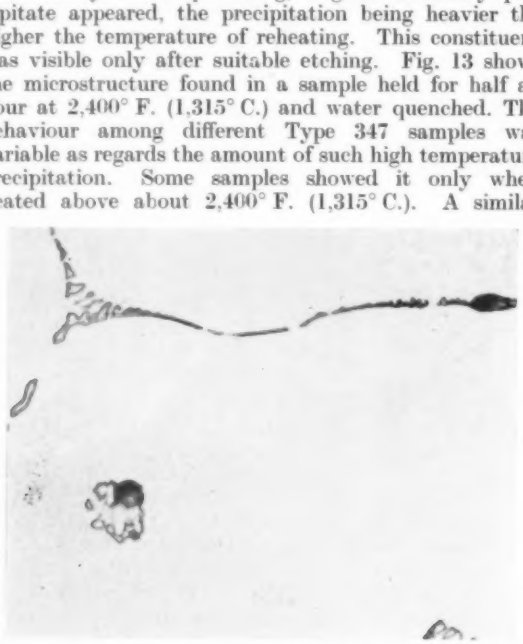


Fig. 15.—Plate, quench-annealed 2,500° F. (1,370° C.): eutectic colonies associated with fine grain-boundary precipitate. Electrolytically etched in 10% NaCN for 30 seconds. × 1,500

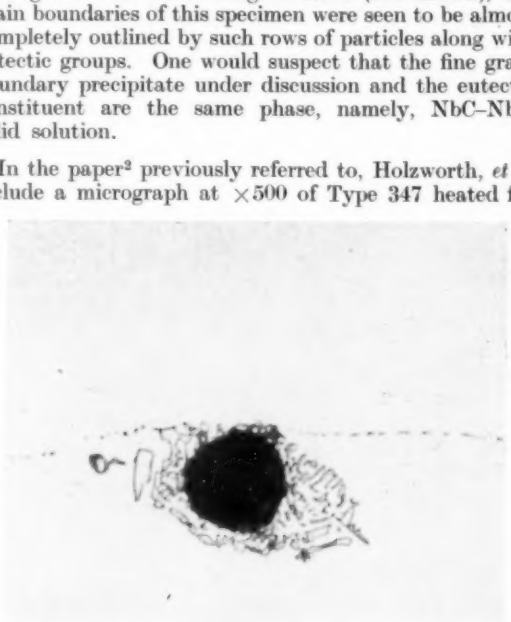


Fig. 16.—Plate, quench-annealed 2,500° F. (1,370° C.): eutectic colonies associated with fine grain-boundary precipitate. Electrolytically etched in 10% NaCN for 30 seconds. × 1,500

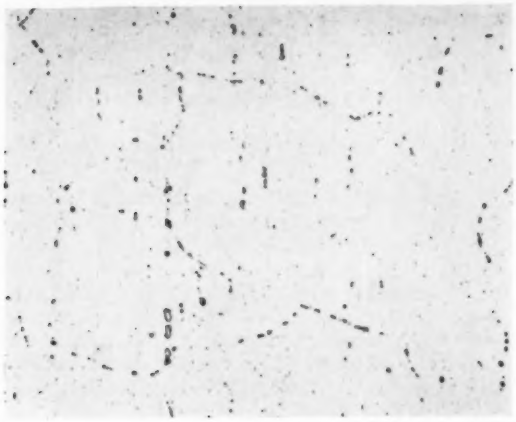


Fig. 17.—Plate, quench-annealed 2,200° F. (1,205° C.) and reheated 1,200° F. (650° C.): moderate precipitation of grain-boundary carbide. Electrolytically etched in 10% NaCN for 5 minutes. × 250

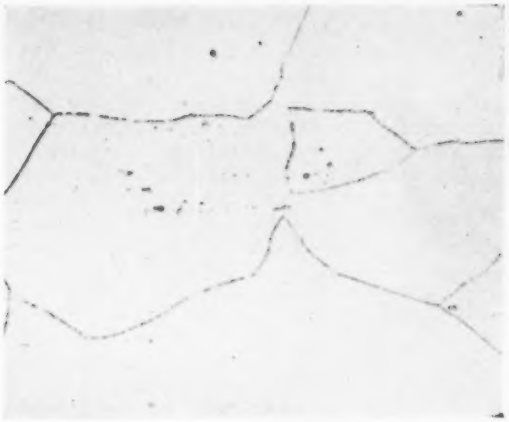


Fig. 18.—Plate, quench-annealed 2,300° F. (1,260° C.) and reheated 1,200° F. (650° C.): heavy precipitation of grain-boundary carbide. Electrolytically etched in 10% NaCN for 4 minutes. × 250

half an hour at 2,500° F. (1,370° C.). The structure shown in their micrograph and the structure of the samples heated at 2,500° F. (1,370° C.) by the present author are very similar when the latter are viewed at ×500. The writer confirms their finding that 18–8 type stainless steels without niobium do not develop a grain boundary constituent when heated at 2,500° F. (1,370° C.). Corrosion tests, in boiling 65% nitric acid, conducted by Holzworth and co-authors showed a very low rate of attack for Type 347 quench-annealed from 2,400° F. (1,315° C.). The writer would expect that their corrosion sample contained some of the grain boundary precipitate being discussed and therefore the indications are that it does not decrease corrosion resistance in at least some highly corrosive media.

(*b*) *Developed in the Range* 850°–1,650° *F.* (455°–900° *C.*).

As reported by other authors and confirmed by the present work, if 18–8Nb stainless steel is heated at temperatures sufficiently high to dissolve the dispersed niobium "dot" carbide, grain boundary precipitation of what is believed to be carbide rich in chromium can occur upon reheating in the sensitisation temperature range, or during retarded cooling from the high temperatures. Cooling conditions most likely to result in grain boundary precipitation would be those where the rate of cooling is fairly rapid through temperatures above 1,600° F. (870° C.), where carbon precipitates as niobium carbide, and then slow cooling through the range where chromium-rich carbide may form.

Samples of ¼-in. plate of Steel C were treated as shown in Table II. Each sample was given only the treatments indicated, in turn from top to bottom, followed by water quenching.

TABLE II.—EFFECT OF OVERHEATING ON SENSITIVITY TO GRAIN BOUNDARY PRECIPITATION.

Specimen No.	1	2	3	4	5	6	7
Heated 30 min. at 2,300° F. (1,260° C.)							
Heated 30 min. at 2,200° F. (1,205° C.)		•	•	•	•	•	•
Heated 30 min. at 2,100° F. (1,150° C.)	•						
Reheated 3 hr. at 1,600° F. (870° C.)			•	•		•	•
Reheated 3 hr. at 1,200° F. (650° C.)	•	•		•	•		•
Grain boundary precipitation*	N	M	N	N	H	N	L

* N, none; L, light; M, moderate; H, heavy.

The structures of Specimens 2 and 5 are shown in Figs. 17 and 18. It was found that with different lots of 18–8Nb steel the precipitation effects noted in the table may occur with higher or lower initial temperatures of heating.

As an extra precaution to assure substantially complete precipitation of carbon as dispersed niobium carbide, it is sometimes recommended that hot working or quench-annealing of 18–8Nb be followed by a "stabilising" heat treatment within the range 1,550°–1,650° F. (840°–900° C.). Although it has been commonly recommended that temperatures anywhere in this range are suitable, one would expect that using the high side of the range would offer greatest assurance that no chromium-rich carbide will precipitate. Specimens 4 to 7 demonstrate that a 1,600° F. (870° C.) stabilising treatment is beneficial when overheating has occurred during annealing but is only partially effective when overheating has been very severe (see Specimen 7). Specimen 7 showed no grain boundary precipitate "as quench-annealed" from 2,300° F. (1,260° C.). Reheating near 2,000° F. (1,095° C.) after the 2,300° F. (1,260° C.) treatment and prior to the 1,600° F. (870° C.) treatment would probably further decrease the susceptibility to grain boundary precipitation upon reheating at 1,200° F. (650° C.). Of course, the proper precaution is to avoid overheating, and then, when sufficient niobium is present, a stabilising heat treatment is of little or no benefit and may even be harmful[3]. The A.I.S.I. and S.A.E. standard chemical specification for wrought materials calls for a minimum niobium content of ten times the carbon and the Alloy Casting Institute standard calls for a minimum content of eight times the carbon. For more "fool-proof" immunity, Rosenberg and Darr[3] have suggested a minimum of twelve times the carbon.

After the treatment shown in Table II, Specimens 2 and 5 were reheated one hour at 2,000° F. (1,095° C.), followed by water quenching, and this did not effect complete solution of the grain boundary phase. Dispersed precipitation of carbide within the grains occurred.

3 "Stabilisation of Austenitic Stainless Steel," by S. J. Rosenberg and J. H. Darr. *Transactions, American Society for Metals*, **41**, 1949, 1261 to 1288.

(*c*) *In Zone Adjoining a Weld.*

The experiments described above give insight into what occurs in parent metal affected by the heat of welding. If welded Type 347 is subsequently reheated in the sensitisation temperature range, grain boundary carbide precipitation will occur in the narrow zone, immediately adjoining the weld, which had been heated during welding to temperatures above about 2,300° F. (1,260° C.). The paper by Holzworth, *et al*[2] is a thorough investigation of what occurs at welds in 18–8Nb steel. As mentioned above, under some circumstances a high temperature grain boundary precipitate may possibly form during welding, in the parent metal next the weld.

That the zone immediately adjoining a weld in Type 347, after a sensitising heat treatment at or near 1,200° F. (650° C.) is prone to high rates of corrosive attack, has been reported by Scheil[4, 5], Brown[6], Fontana[7] and Holzworth *et al*[2]. The phenomenon has been variously referred to as "knife-line attack," "grooving," and "channelling." Welded Type 321 stainless (18–8 Ti) is also subject to knife-line attack and for the same reasons.

4 M. A. Scheil, in General Discussion, "Symposium on Evaluation Tests for Stainless Steels." A.S.T.M. Special Publication No. 93, 1950, p. 228.
5 M. A. Scheil, "Conservation of Columbium". *Metal Progress*, **58**, November, 1950, 699.
6 M. H. Brown, same source as reference 4, p. 224.
7 "Corrosion," by Mars G. Fontana. *Industrial and Engineering Chemistry*, **42**, 11, 1950, 99a to 100a.

Conclusion

Niobium-stabilised 18–8 steels are not "fool-proof" and improper processing procedure can result in grain boundary carbide precipitation which may make the steel susceptible to intergranular corrosion. However, as was repeatedly emphasised in the symposium given in Reference 4, "susceptible" material may or may not corrode intergranularly, depending upon specific testing or service conditions. The deficiencies of improperly processed material may only become apparent under relatively severe conditions of service.

Acknowledgment

The author is indebted to Mr. C. M. Webster for the photomicrographs appearing in this paper.

New and Revised British Standards

GLOSSARY OF TERMS (WITH SYMBOLS) RELATING TO THE WELDING AND CUTTING OF METALS. (B.S.499 : 1952). PRICE 21s.

THE considerable increase in the application of welding which resulted from the war, and the many new techniques developed since the 1939 edition of B.S.499, have necessitated a much more comprehensive treatment of the subject than was given previously. In view of the magnitude of the subject it was decided to divide the Glossary into a number of sections dealing respectively with :—

(*a*) Terms common to most types of welding.
(*b*) Welding with pressure.
(*c*) Fusion welding (welding without pressure).
(*d*) Brazing and bronze welding.
(*e*) Testing.
(*f*) Weld imperfections.
(*g*) Scheme of symbols.
(*h*) Cutting.

The largest sections are naturally those relating to welding with pressure and to fusion welding. These, like the other sections, deal fully with the terminology applicable to the techniques and equipment. The separate section on testing contains many terms which have an application to diverse welding practices and by giving greater prominence to preferred terms it encourages general use.

The scheme of symbols in Section 7 (which has already been published separately) represent a considerable advance on that given in the appendix to the 1939 edition. As previously announced, this scheme differs radically from former procedure in order to comply with the general move towards achieving greater co-ordination between American, Canadian and British practice which originated at the Ottawa Conference in 1945.

The standard also includes the publication known previously as B.S.449 : Part 2, which deals with those terms relating to imperfections in welds which are appropriate for radiographic examination.

The entire publication is fully illustrated with sketches and line drawings : the section on radiographic examination includes reproductions of radiographs and the scheme of symbols is profusely illustrated with examples showing its application.

FILLER RODS FOR GAS WELDING. (B.S.1453 : 1952) PRICE 3s.

B.S. 1453 was first issued in 1950 under the title of "Steel filler rods for gas welding of mild steel" and covered only one type of rod. This issue was mainly intended to provide a specification for the type of filler rod used in gas welding of pipelines. The 1952 edition is very much wider in scope than the 1950 edition as it covers 31 types of filler rods under the headings of steel, cast iron, copper and copper alloys, magnesium alloys and aluminium and aluminium alloys. Each type is defined in terms of chemical composition. The filler rod specified in the 1950 edition is included in the 1952 edition as Type A2.

SOLID DRAWN COPPER-SILICON TUBES FOR GENERAL PURPOSES. (B.S.1866 : 1952). (PRICE 2s.) THE British Standards Institution recently issued a specification for solid drawn copper silicon tubes for general purposes. The standard gives the chemical composition and mechanical properties and includes details of making the mechanical tests and a mercurous nitrate test. Tolerances on width, length and thickness are tabulated.

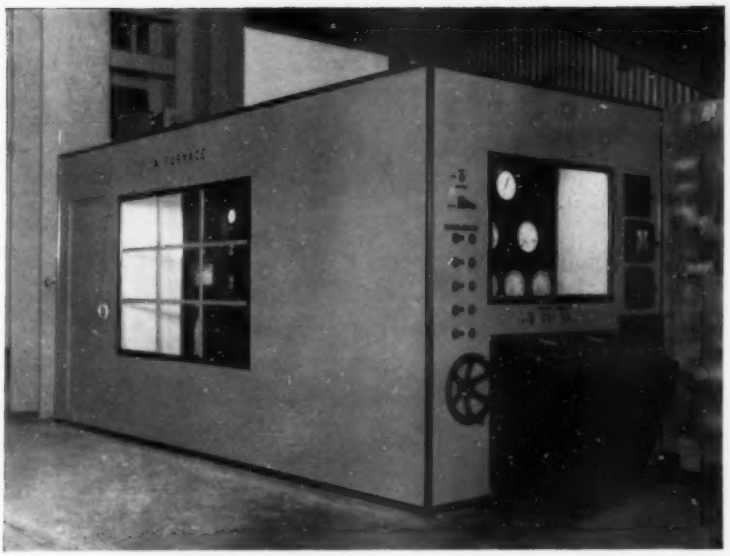
SOLID DRAWN ALUMINIUM BRONZE TUBES FOR GENERAL PURPOSES (7 PER CENT. ALUMINIUM). (B.S.1867 : 1952) PRICE 2s. 6d.

THIS standard gives the chemical composition and mechanical properties and includes details of making the mechanical tests and a mercurous nitrate test. Tolerances on width, length and thickness are tabulated.

Copies of these standards may be obtained from the British Standards Institution, Sales Branch, 24, Victoria Street, London, S.W.1.

Automatic Control of Open Hearth Furnaces

Comprehensive Installation at Shotton



Pressurised control cubicle in which the measuring instruments and automatic controllers are accommodated.

UNTIL comparatively recently, the first hand melter on an open hearth steel furnace had to rely mainly on his judgment and experience in controlling the furnace. The post-war demand for increased productivity, with economies in fuel, emphasized the shortcomings of such a situation, and it is safe to say that the increased output obtained during the last few years would have been impossible of achievement had it not been for the progress in steel plant instrumentation which has taken place. By the aid of roof temperature pyrometers, for example, it has been possible to drive furnaces harder without the danger of failure of the roof, and with measuring and control instruments applied to the fuel system, more efficient use of gas and oil has been ensured.

The installation at the new steel plant at the Shotton Works of Messrs. John Summers & Sons, Ltd., is the result of development work carried out by Messrs. Tinsley (Industrial Instruments), Ltd., in close collaboration with the steel company, and is claimed to be the most comprehensive automatic control scheme yet to be installed on an open hearth furnace plant in this country.

The plant consists of eight fixed furnaces, each of 150 tons capacity, designed for mixed fuel firing (fuel oil and coke-oven gas). Each furnace is provided with a control cubicle in which the measuring instruments and automatic controllers are accommodated. These control cubicles are pressurised to prevent the ingress of the dust-laden steelworks atmosphere, and each contains two instrument panels, at right angles to each other, which are viewed through glass windows at the sides of the cubicle.

The Instrument Panels

One panel is mounted on the furnace side of the cubicle and accommodates the following recorders :—

(1) Triplex recorder for oil, steam and gas flows ;
(2) Triplex recorder for the roof temperature at three points on the furnace crown ;
(3) Triplex recorder for furnace pressure and air flow : the third recorder in this unit is used as a spare ;
(4) recorder for oil and steam temperatures ;
(5) recorder for checker temperatures ;
(6) recorder for liquid steel temperatures ;
(7) four integrators for oil, steam, gas and air ;
(8) clock ; and
(9) two pressure gauges showing the oil pressures in the two oil systems which provide the motive power for the controller and automatic reversal unit.

The second instrument panel, which is viewed through a window at one end of the cubicle, accommodates the following indicators :—

(1) indicators for oil, steam, gas and air flows, and for heat flow (the total heat flow of the furnace on mixed firing) ;
(2) indicator for furnace pressure ;
(3) indicator for gas temperature ; and
(4) three indicators for roof temperatures at three points on the furnace crown.

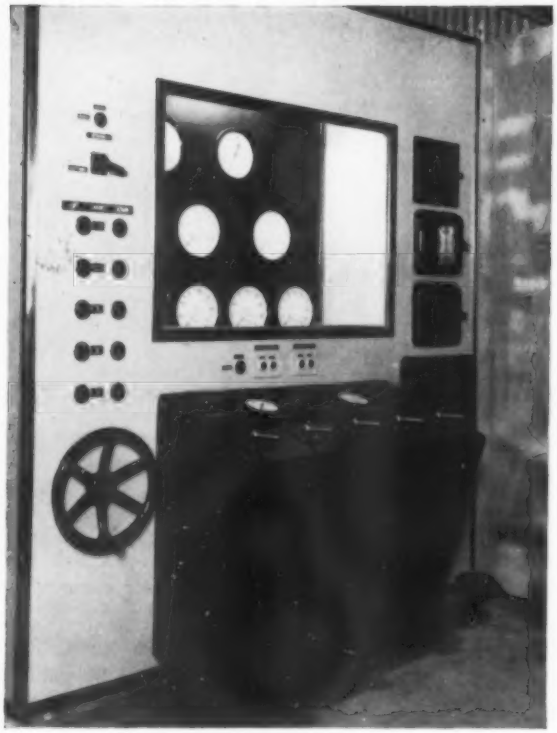
Below this window is a desk on which are mounted the hand control valves used for switching the various circuits from automatic to hand control, and for the remote operation of the various control organs by hand. Two gauges, showing the oil and steam pressures in the mains to the burners are also mounted on the desk.

With this layout, the furnace operator standing at the control desk can see the furnace and the indicators, and can conveniently operate all the controls necessary for running the furnace. On this end of the cubicle are also mounted the various control point settings, push buttons for raising and lowering the furnace doors, and the switch to initiate the reversal cycle.

Automatic Controllers

The following automatic controls are incorporated in the control scheme :—

Maximum Controller.—This instrument has two functions : during the charging period, when the roof



Control desk end of cubicle with temperature, pressure and flow indicators.

temperature is low, it maintains the heat input at a pre-set maximum value, whilst at the end of the charging period, and during the refining period, it controls the roof temperature at the desired maximum value. The change-over from maximum heat input control to maximum roof temperature control is completely automatic. Roof temperature is measured by three partial radiation pyrometers sighted on to the furnace roof through holes in the back wall, and recorded and indicated on the instrument panels. The maximum of these three temperature signals is selected continuously and automatically and used to actuate the maximum controller, which is provided with a unit to prevent an over-shoot in temperature immediately after reversal.

Oil/Steam Ratio Controller. — This instrument regulates the steam flow to the furnace to maintain the desired oil-flow/steam-flow ratio. It is fitted with a zero setting unit to give a variable flow ratio over the flow range—the ratio is altered to give a larger proportion of steam as the oil flow is reduced, and in this way the velocity at the burner is maintained to obtain efficient atomising.

Oil/Gas Ratio Controller. — This instrument adjusts the coke-oven gas flow to maintain the required oil-flow/gas-flow ratio.

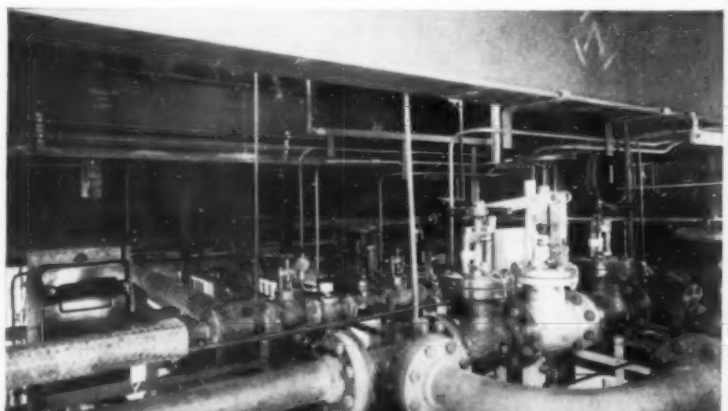
Fuel/Air Ratio Controller.—This instrument adjusts the combustion air flow to the furnace to maintain the air flow in the required ratio of the total fuel flow to the furnace. It is calibrated to provide sufficient combustion air for both oil and coke-oven gas.

Furnace Pressure Controller.—The furnace pressure is measured at the centre of the roof crown by a null-balance pressure detector, the output of which is transmitted to the indicator and recorder panels. This signal is also transmitted to the instrument which controls the furnace pressure by positioning a louvre damper at the outlet of the waste-heat boiler fan, and by controlling the speed of the latter. The damper works from the fully-open to the half-open position, and the waste-heat boiler fan speed is adjusted so that the required furnace pressure can be obtained when the damper is set at some position in this range. This form of control results in a saving in the power consumed by the waste-heat boiler fan as it prevents excessive throttling of the flow at the fan outlet.

Automatic Reversal Unit.—The furnace is reversed automatically when the operator throws the reversal switch mounted adjacent to the control desk. This action initiates the reversal cycle in which the oil, steam, air, waste gas and coke-oven gas valves are operated in the correct sequence. The reversal unit, which is accommodated in the control cubicle, consists of a motor which drives a horizontal shaft on which are mounted a series of cams. These cams, specially cut to give the correct timing sequence for the reversal, operate hydraulic pilot valves coupled to hydraulic cylinders which, in turn, operate the reversal valves and limit switches for the various electrical circuits. The oil, steam and coke-oven gas valves are operated hydraulically, whilst the air and waste gas dampers are operated electrically. Should the reversal motor fail, a hand wheel is provided so that the operator can turn the cam shaft by hand.

Flow Metering.—The oil, steam, gas and air flows are measured by meters mounted on the valve platform

continued on page 38



The oil, steam, gas and air flows are measured by flow meters mounted on the valve platform below stage level.

An Examination of Joule's Work on the Metallurgy of Amalgams

By H. J. Axon, B.Met., D.Phil.

Metallurgy Department, the Victoria University of Manchester

Joule's metallurgical experiments have been largely overshadowed by his work on the mechanical equivalent of heat, and it is probable that few metallurgists have even heard of them. In this article, his work on the constitution of binary alloys of mercury is reviewed in the light of modern knowledge.

THE researches of Joule on the mechanical equivalent of heat are known to all students of science, but it might be of interest to metallurgists to draw attention to the fact that Joule also concerned himself with certain topics of immediate metallurgical interest. The standard reference book on the constitution of binary alloy systems (Hansen: "Der Aufbau der Zweistofflegierungen") contains a brief mention of Joule in connection with early work on the amalgam alloys of the systems mercury-iron, mercury-copper, mercury-silver, mercury-platinum, mercury-zinc, mercury-lead, and mercury-tin. Hansen also gives references to the *Chemical Gazette* of 1850, and to the *Journal of the Chemical Society* of 1863 and 1876, in which Joule published his work on amalgams. There is also a paper in the second volume of the third series of the Memoirs of the Manchester Literary and Philosophical Society in which these researches are reported.

Mercury-Iron System

Joule was led to the study of amalgams by his wish to produce a perfectly true and polished metallic surface, since he thought that by depositing iron onto a mercury cathode he would get a plate of iron possessing a smoothness equal to that of the fluid mercury. He conducted this experiment using a Daniell cell as the source of E.M.F., with a mercury cathode, iron anode, and ferrous sulphate electrolyte. He reported that the iron anode gradually dissolved whilst an equal portion of iron was deposited in the mercury, causing it to lose its fluidity until it finally appeared crystalline. The iron lost very little of its "magnetic virtue" by combination with the mercury, and an amalgam of iron when left under water for a few days became coated with rust. Joule considered the possibility that the iron and mercury might combine together to form a binary compound, and he tested this idea by analysing specimens of amalgam from which he had removed as much surplus mercury as possible by the application of pressure. The general method of analysis was to heat the amalgam in a glass tube through which a current of hydrogen was passed, the mercury being distilled off, leaving the other metal. Joule concluded that the solid amalgam of iron which contained the largest quantity of mercury was a binary compound of the two metals. Later work has failed to confirm the existence of binary iron-mercury compounds, and it is obvious that Joule's "solid amalgam containing the largest possible amount of mercury" was simply a solid sponge of metallic iron with mercury trapped within the pores.

Mercury-Copper System

Binary amalgams of copper, silver, platinum, zinc, lead, and tin, were also prepared by electrodeposition of the metal onto a mercury cathode, and the resulting amalgams were subjected to hydraulic pressure to remove excess mercury. The solid amalgams so produced, which contained a maximum quantity of mercury, were analysed, and, by assuming either that some of the excess mercury had not been removed by pressure, or that the supposed compound had decomposed under pressure, Joule was able to convince himself of the existence of binary compounds in all these amalgam systems. Of the amalgams of copper, for instance, he wrote: "It will appear that a moderate pressure continued for a short time leaves a binary compound of the metals along with a quantity of mercury which may be supposed to be entangled among the crystals. When the pressure was very great, or was continued for a long time, the resulting amalgam invariably contained more than one equivalent of copper. I believe that this arises from a decomposition of the binary amalgam by the violent mechanical means adopted." Later work on copper-mercury alloys has suggested the existence of a binary compound of formula CuHg which is stable up to 96° C. If we adopt modern values of atomic weights we find that in the compound CuHg, 100 parts of mercury are associated with 31·7 parts of copper, whereas Joule's results gave 100 of mercury associated with about 30 of copper. The actual values for medium and high pressures were in the range 28·4 to 35·6 of copper. Thus it would seem that in the copper-mercury system, Joule did produce almost pure samples of the compound CuHg by applying a medium hydraulic pressure to partially fluid amalgams. There are, however, four interesting cases in which Joule's results do suggest the decomposition of the binary compound. In these four cases he found that 100 parts of mercury were associated, respectively, with 39·02; 38·43; 40·18; 44·34 of copper. In view of the absence of complete experimental details, on the one hand, and the experimental scatter of the results, on the other, it does not seem profitable to discuss these exceptions in detail, but they are suggestive, and it would probably be worth while to repeat these experiments.

Mercury-Silver System

In his experiments on alloys of silver and mercury, Joule reported that, on making the analysis, it was found necessary to employ a temperature nearly sufficient to fuse the silver in order to drive off the last trace of mercury. This observation is in accord with the extensive solid solubility of mercury in silver which has been suggested by later work. The modern form of the equilibrium diagram also suggests the presence of two intermediate compounds, both with a slight range of composition. The compound with the greater proportion of mercury decomposes at 127° C. and is based on a composition of 70% mercury by weight, which would correspond to 100 parts of mercury to 43 of silver. Joule's mean value for the composition of the amalgam, after being pressed at 72 tons/sq. in., was 43·71 of silver to 100 of mercury. This is in excellent agreement with the probable composition of the pure compound, and suggests that the compressed amalgams were composed of essentially pure crystals of compound. It is, however, instructive to examine the individual results in more detail, since this gives an idea of the experimental scatter involved :—

	Mercury	Silver
72 tons for 1 hour.. ..	100	40·13
72 tons for 1½ hours ..	100	40·00
72 tons for 1½ hours ..	100	51·55
72 tons for 20 mins. ..	100	43·15

It is to be noted that although these results give a mean value of 43·71 parts of silver to 100 of mercury, yet the two apparently identical experiments in which the pressure was applied for 1½ hours give widely different results. Joule's own conclusion, that " allowing for mercury remaining in an uncombined state, we may conclude that the solid amalgam containing the largest quantity of mercury is composed of one equivalent of silver to two of mercury " is not strictly correct, but his numerical values do suggest that he produced almost pure specimens of the compound based on 70% mercury.

Mercury-Zinc System

A consideration of the alloys of mercury and zinc is less straightforward, since in this system two compounds have been suggested, both having a range of composition. The one which contains most mercury is based on 60% by weight of mercury and decomposes at 20° C., whilst the other is based on 55% mercury and decomposes at 43° C. Slight variation of room temperature about 20° C. would be expected to control the composition of the compound which is in equilibrium with the fluid mercury. Three results are available for an amalgam after compression at 50 tons/sq. in. for one hour, the amounts of zinc associated with 100 parts of mercury being 76·7 ; 79·6 and 75·9. These values are greater than the value of 66 which would be expected from the compound which contains most mercury and which decomposes at 20° C., but are near to the value of 81 expected of the other compound which is richer in zinc. It would therefore appear that if Joule's mercury-zinc specimens were composed almost entirely of crystals of compound, without free mercury, then that compound was the compound of higher melting point. This suggests either that Joule's experiments were conducted at a temperature higher than 20° C., or that the application of pressure had caused the low melting point compound to decompose in favour of that which is stable to a higher temperature.

Mercury-Lead and Mercury-Tin Systems

Only one experiment appears to have been conducted on the mercury-lead system, compression under a pressure of 3 tons/sq. in. for one day resulted in a mass of bright crystals, easily fractured, which was composed of 100 parts of mercury to 194 of lead. Joule concluded that in this case the pressure had partly decomposed the binary compound. More recent work on the equilibrium diagram of the mercury-lead system suggests that compounds might possibly exist at temperatures below −37° C., but at room temperature the equilibrium phases are a liquid solution of lead in mercury and a solid solution of mercury in lead, this solid solution containing 33% of mercury at room temperature. The limit of this solid solution corresponds to 100 parts of mercury with 201 parts of lead, figures which are in close agreement with Joule's and which suggest that his experiments had produced crystals of the equilibrium solid solution without any appreciable excess of free mercury. Similar remarks apply to the system mercury-tin, in which Joule found 100 parts of mercury associated with approximately 400 parts of tin. No compounds exist in this system at room temperature, and although the limit of solid solubility of mercury in tin is not accurately known, it appears to be about 20% at room temperature, which agrees well with the proportions found by Joule.

General Considerations

Joule interpreted all his results in terms of the formation and decomposition of binary compounds. In this he was not strictly correct, but it is interesting to see that, apart from the system mercury-iron, his results can be interpreted in terms of established features of the appropriate equilibrium diagrams. In some cases these features are actually compounds, though not of the exact composition suggested by Joule, and in other cases are saturated solid solutions.

The possibility of the decomposition of compounds under pressure, particularly in the case of mercury-zinc, is suggested, but the scatter of the experimental results is too great to prove this point. Further investigation of this matter might prove interesting.

The outstanding difficulty in discussing this work is the obviously erroneous result obtained for the mercury-iron system, but a study of the rather meagre experimental details provides a possible solution. Joule appears to have conducted much more careful and extensive experiments on the amalgams of copper, silver, zinc, lead, and tin than on the amalgams of iron. Indeed, in the case of mercury-iron alloys, only two compression experiments were conducted, both of which are reported as " Compressed rapidly with a force of 50 tons on the square inch " and giving results of 79 and 103·2 parts of iron, respectively, to 100 of mercury. It seems possible that the pressure was not applied for a sufficiently long time to expel all the uncombined mercury. This would explain not only the marked difference of iron content noted above, but also the fact that a further specimen, which was prepared without the application of pressure, contained 127·6 parts of iron to 100 of mercury. In all the other alloy systems the pressure was applied for a stated period of time and in general seems to have removed most of the uncombined mercury.

A Sterling Silver Containing Aluminium

By G. E. Gardam, Ph.D.

Design and Research Centre for the Gold, Silver and Jewellery Industries.

The use of copper as a hardening agent for sterling silver results in a defect known as "firestain" when the material is annealed or hard-soldered. It has been found that the addition of a small percentage of aluminium prevents this trouble, and at the same time inhibits grain growth and confers on the alloy enhanced precipitation hardening properties.

SILVER articles for decorative, domestic and table use are prized not only because of the intrinsic value of the metal and its inherent beauty, but also because of its non-toxic nature and its relative incorrodibility by foodstuffs. Owing to its great workability, silver can be wrought into complicated forms with simple tools by skilled craftsmen. It has long been appreciated, however, that unalloyed or "fine" silver is too soft to withstand normal usage; it has, therefore, been the practice to add a proportion of base metal, traditionally copper, to harden and strengthen it. Because the temptation to use unnecessarily large additions of base metal is obviously great, legislation has existed from remote times specifying the minimum silver content of articles offered for sale as silver. This minimum content was fixed at 92·5% in this country, certainly before A.D. 1189, and Saxon pennies were of a composition so near this value,[1] considering the capability of the times, as to suggest it was established earlier. Enforcement of the standard by independent assay of every article was entrusted by Edward I, to the Worshipful Company of Goldsmiths of the City of London in A.D. 1300 and has been carried out continuously since that time at their Hall (hence "hall-mark"), and subsequently, by other Assay Offices also. Each article is separately sampled (in several places if it is built up from parts) and the sample analysed for silver. If the assay is satisfactory, the article is impressed with four marks—the quality mark, which for silver is a lion, the hall-mark, showing which particular assay office certifies the quality, a date letter and a manufacturer's mark. It may be added that rejected articles are not merely returned, unmarked, but are irretrievably deformed by the Assay Office before return to the owner!

The legislation is silent on the base metal constituent, but long experience had convinced craftsmen that, of those metals available to them in former times, copper was the most convenient. Modern silversmiths adhere to this composition for "standard" sterling, although sometimes a small proportion of the copper is now replaced by cadmium to attain even greater ductility.

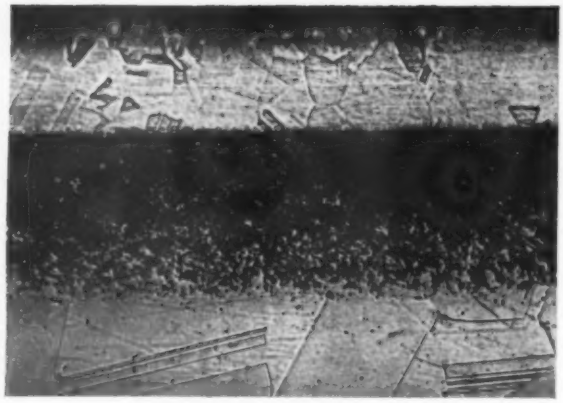
The Defect of Firestain in Standard Sterling Silver

Some sterling silver articles are cast, notably small details such as knobs, feet, handles, etc., but the great majority of articles are wrought from rolled sheet. Traditionally this was done by "hand raising" (i.e., hammer beating)—a process still much used—but for quantity production the more rapid and mechanised processes of deep drawing, spinning, and, especially, drop stamping, are preferred.

In all these processes a number of stages are usual, with intermediate annealing. Furthermore, the constituent parts are finally assembled together by hard-soldering with a silver-rich alloy whose composition and melting point is very little below that of sterling silver. Much of the annealing and all the soldering is effected with the flame of a coal-gas-air blowpipe; the oxidising or reducing nature of the flame and the temperature of the article are controlled only by the skill and experience of the silversmith. Silver does not oxidise when strongly heated in air, but the copper is oxidised to cuprous or cupric oxide. Thus a layer of pure silver interspersed with copper oxide is formed. The pure silver is easily permeated by oxygen, so that the copper of deeper layers is then oxidised. Thus, depending on the time and temperature of heating, the copper, to a greater or less depth, is converted to copper oxide, although the silver matrix maintains the metallic coherence. Pickling of the oxidised surface, for example in dilute sulphuric acid, removes the superficial, but not the deeper seated, copper oxide, so that the surface consists of fine or unalloyed silver covering a layer of silver-copper oxide mixture. Successive annealing, cold working and pickling processes thus produces a surface which, when lightly polished, exhibits the pure white lustre of silver although heavier polishing reveals dark and disfiguring stains. These are traditionally known as "firestain" or "fire." This condition existed in the sheet silver as rolled, until close-annealed "fire-free" silver was made available.

In much antique silver the unalloyed silver layer is indeed so thick that the disfiguring oxide is only reached after generations of periodical cleaning. This explains the alleged "mellow" appearance of much old family and institutional plate.

By starting with fire-free sheet, and by reducing the number and severity of the annealing operations to a minimum for economic reasons, the modern silversmith reduces the thickness of the superficial layer of fine silver. He therefore finds it essential to remove the whole of the firestained layer by fairly heavy abrasion, or more often, by anodic electrochemical stripping in a cyanide-ferrocyanide solution. Either of these processes wastes the expensive alloy; the former is laborious, whilst the latter roughens the surface and thus necessitates more vigorous polishing than would otherwise be necessary. A third method of dealing with the trouble, viz., by covering it with an electroplated coating of silver, is widespread, but it is open to severe criticism on ethical grounds.



Reduced ⅔ linear in reproduction

Fig. 1.—Cross-section of a piece of sterling silver after annealing. A layer of firestained standard sterling silver 0.004 in. thick can be seen in the centre between a protective layer of electroplated silver and the unharmed sterling silver. × 300 (approx.)

The Rate of Formation of Firestain

The rate of penetration of oxidation into standard sterling was studied to some extent by E. Raub and M. Engel[2], but the results are not very useful for the present purpose. It was, therefore, necessary to obtain further information; the experiments were conducted as follows:—

Pieces of standard sterling silver sheet, ½ × ¼ × 0·036 in. were placed individually on a large metal block in the uniform temperature zone of an open ended tubular furnace, at such time intervals that when all were quickly removed and quenched together the individual specimens had been at the temperature for 1, 2, 4, 8, 16 and 32 minutes respectively. The specimens were so small relative to the large metal block, that they attained the constant temperature very rapidly; separate experiments were performed at 600°, 650°, 700° and 750° C. The specimens were then silver plated without etching—a technique which was made possible by the fine silver rim and the absence of silver oxide—and the plated specimens mounted in Diakon, sectioned, polished, etched and examined. The quenching after heat treatment produced a single phase structure and rendered subsequent examination easier. The depth of penetration of oxygen was quite sharply defined (Fig. 1) and was measured in several places on each specimen. Graphs of the average results are shown in Fig. 2. Similar results, obtained when steam was blown through the furnace, are shown in Fig. 3. In these experiments no attempt was made to ensure that all the air was replaced by steam, but the conditions were intended to simulate the well-known method of minimising firestain by annealing in a "wet" atmosphere. The curves in both cases are approximately exponential in shape.

It might be thought that the time and temperature of annealing necessary to remove work hardness is too short for deep penetration of firestain. This is indeed supported by Fig. 4, which shows the hardness of hard-rolled standard sterling silver sheet after annealing for various times and temperatures. These figures were obtained by the method previously described, except that rapid air cooling was substituted for quenching. It will be apparent that a temperature of 650° C. and a

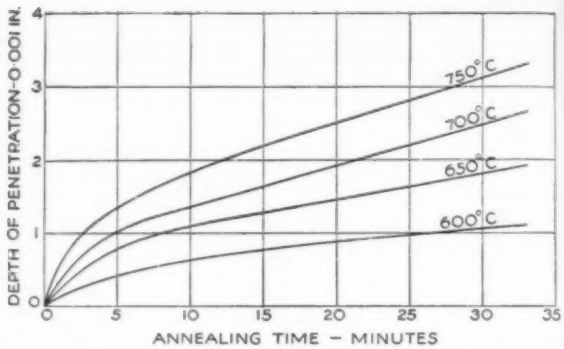


Fig. 2.—Graph showing rate of penetration of firestain into standard sterling silver (annealed in air), and the variation with temperature.

time of four minutes is adequate to remove almost all work hardness; the depth of penetration of firestain under these conditions is slight. Nevertheless, the craftsman actually extends the time to ensure that all portions of the article attain an adequate temperature. Furthermore, when the method of heating is by coal-gas-air blowpipe, the only method of temperature measurement is by colour. Since the dullest perceptible red heat is about 600° C. there is obviously grave danger of exceeding the minimum safe temperature.

The process of hard-soldering the various component parts of the article together is, however, a more frequent cause of deep firestain. Because a succession of joints may need to be made on the same article, the craftsman uses successive solders of different melting points as exemplified in Table I.

TABLE I.—COMMERCIAL SILVER SOLDERS.

Trade Term	Liquidus	Solidus	Brinell Hardness	U.T.S. tons/sq. in.
Easy	723°	705°	121	28
Medium.. ..	765°	720°	110	25
Hard	778°	745°	120	27
Enamelling ..	800°	730°	110	25
Eutectic ..	778°	778°	90	22

The hall-marking authorities encourage the use of solders of as high silver content as possible, and therefore of high melting point. The technique of hard soldering involves heating the whole article up to the melting point of the solder and above that of the borax flux (m.p. 741° C.). The heating up, "flushing" of the solder and subsequent cooling occupies some few minutes and

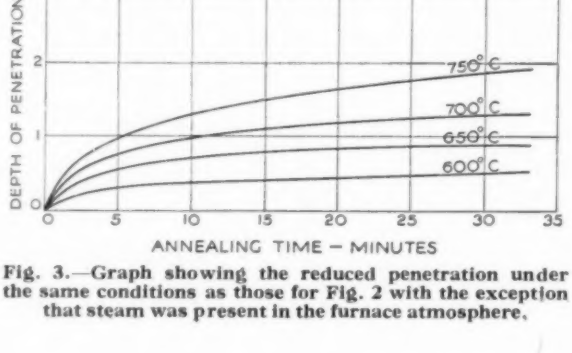


Fig. 3.—Graph showing the reduced penetration under the same conditions as those for Fig. 2 with the exception that steam was present in the furnace atmosphere.

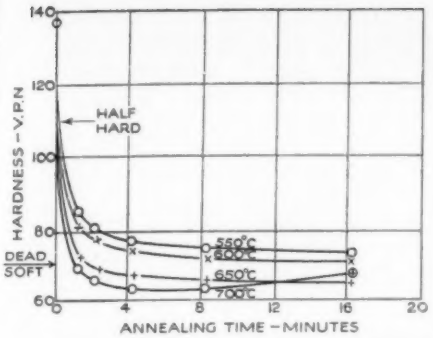


Fig. 4 (left).—Graph showing the effect of temperature on softening of standard sterling silver by annealing.

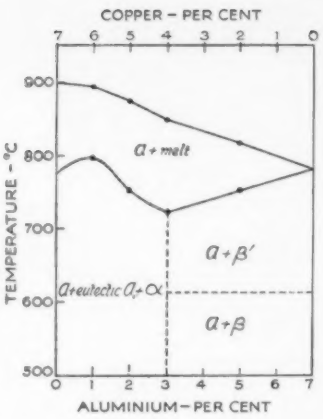


Fig. 5 (right). — Ueno's diagram for the silver 93% section of the silver-copper-aluminium ternary diagram. (This is a copy of Ueno's diagram and the nomenclature of the phases is his.)

may need to be repeated several times for successive joints on the same article. Thus, because of the high temperature reached, the soldering operations are much the most productive of deep firestain, and they can hardly be carried out in a controlled atmosphere, except in the largest scale production.

An Improved Sterling Silver Alloy[3]

It has been found that sterling silver alloys (i.e., those containing more than 92·5% silver) which contain more than a critical percentage of aluminium, with the balance as copper, form a surface film of aluminium oxide on heating, which effectively prevents penetration of oxygen.

Up to about 0·8% aluminium the alloys oxidise subcutaneously (i.e., form firestain) in a similarly progressive manner to standard sterling. Indeed there is much evidence[4] that on continued heating the aluminium oxidises in situ and causes an irreversible hardening of the alloy. With aluminium contents between about 0·8% and 0·9%, the oxidation is not uniformly progressive ; at certain points it extends into the depth of the metal in a roughly semi-circular (or probably hemispherical) form, whilst on the remainder of the surface the oxide film remains quite thin. At aluminium contents of, or above, 1% the oxidation is purely superficial, and independent of the time of heating ; it can be readily removed by polishing and, in contrast to firestained standard sterling, once the thin outer scale has been removed, the metal is quite sound.

For industrial use an aluminium content of 1·0% to 1·3% has been suggested ; aluminium contents exceeding 1·5% perceptibly affect the colour of the alloy, the strength being increased to an extent viewed unfavourably by hand silversmiths.

Constitution of Sterling Silver Containing Aluminium

The ternary constitutional diagram of the system, silver-copper-aluminium has been examined by S. Ueno[5] who has, fortunately, investigated the 93% silver section. (Owing to the vigilance of the hallmarking authorities in rejecting any articles containing less than 92·5% silver, bullion dealers invariably maintain the silver content slightly above this figure, and approaching 93%, to allow for slight segregation.)

This section, copied in Fig. 5, shows that the alloy 93% Ag, 6% Cu, 1% Al, has a liquidus at 894° C., this being the maximum of the liquidus for the section. The solid which separates is presumably a solid solution of copper and aluminium in silver, but the remaining melt eventually sets to form a second phase.

In accordance with this, it has been found in the present work that when sterling silver containing any amount of aluminium (alloys down to 0·05% Al have been tried) is examined, a second phase is always detected, even after quenching. Rolling the alloy breaks up this second phase, and subsequent heat treatment, with or without quenching, up to a temperature of 780° C. does not influence the shape and pattern of the particles, but above this temperature the second phase is found partially or completely to outline the grains of the matrix. Until this happens grain growth of the matrix crystals does not occur, in contrast to standard sterling silver ; this is a marked advantage of the aluminium bearing sterling silver. Comparison of the structure of quenched and slowly cooled specimens does not show marked growth of the particles of the second phase, though this must undoubtedly occur by rejection of solute from the matrix. Ueno does not show any solid solubility line of the copper-aluminium phase such as occurs in the silver-copper-diagram, but his results show a solidus at 795° C. for 93% silver, 1% aluminium.

Carefully determined cooling curves on an alloy containing 92·5% silver, 6·5% copper and 1% aluminium, show a liquidus at 889° C. and a solidus at 784° C., but no clear evidence of any other change. However, since the solid solubility line of the copper-silver diagram cuts the 92·5% silver section at 750° C. it appears that either the solidus curve falls abruptly between 1% and 0% aluminium, or that there is no sharp solubility curve in alloys containing aluminium.

Precipitation Hardening of Sterling Silver

Silver-copper alloy is a classic example of an alloy which can be hardened by quenching from a high temperature followed by reheating at a lower temperature ; this is due to the possibility of obtaining a single phase structure at 779° C. up to 8·8% silver, and retaining it by quenching. Subsequent reheating at any temperature above 150° C. causes precipitation of a second phase and first a rise in hardness, followed by a fall. This process is not industrially important to silversmiths, for several reasons. In the first place, the statutory limitation of the copper content to 7·5% prevents the full attainment of hardness, which is in any case limited to 150 V.P.N.—rather less than can be attained by cold work. Secondly, the preliminary high temperature treatment, if carried out in air, causes severe firestain.

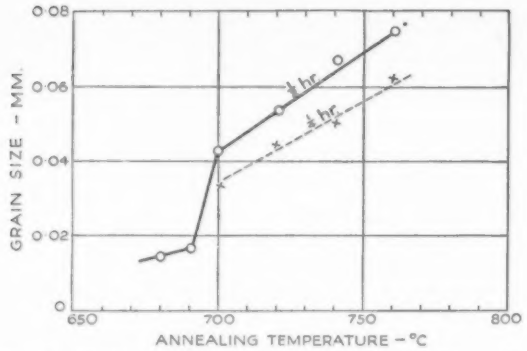


Fig. 6.—Grain size of standard sterling silver after annealing. (Note the sudden increase at 690° C.)

The presence of 1% aluminium in the alloy entirely avoids the second difficulty and the experimental results shown later demonstrate that the maximum hardness and strength obtainable far exceed that produced by cold work alone. The theoretical explanation of this is a matter for discussion. The replacement of some of the monovalent copper atoms by the lighter and moreover trivalent aluminium atoms would be expected to increase the saturation of the lattice, but in fact, as mentioned above, it has been found that a second phase is present in silver-copper alloys containing aluminium, even after quenching from about 780° C.

A further disadvantage of standard sterling silver is the rapid grain growth during annealing or heat treatment at temperatures above 690° C., as shown in Fig. 6. This is liable to cause the well-known surface roughening called "orange peel" on further deformation. Silver articles are invariably polished to a high degree of lustre and smoothness, so that such roughening materially increases the labour of finishing. Sterling silver containing 1% aluminium does not show pronounced grain growth below 780° C. the temperature at which the second phase melts.

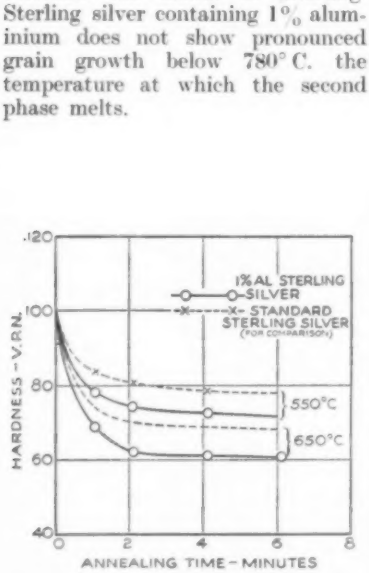


Fig. 8.—Rate of softening of standard sterling silver and the 1% aluminium sterling silver.

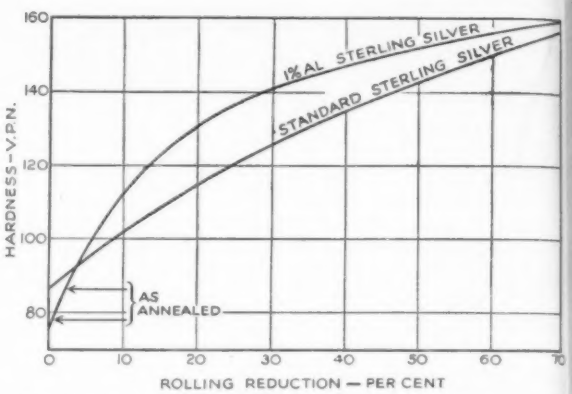


Fig. 7.—Increase in hardness during rolling of standard sterling silver and the 1% aluminium sterling silver.

Properties of Sterling Silver Containing Aluminium

The following results refer to an alloy containing: silver 92·5%, copper 6·5%, aluminium 1·0%. The mechanical properties are not markedly different from standard sterling silver, but the silversmith is extremely sensitive to slight changes.

Work Hardening and Annealing.—It is indicated in Fig. 7 that the work hardening of the alloy containing aluminium is at first more rapid, but later there is less difference; the silversmith usually anneals at 100–120 V.P.N. so that he regards the new alloy as "harder."

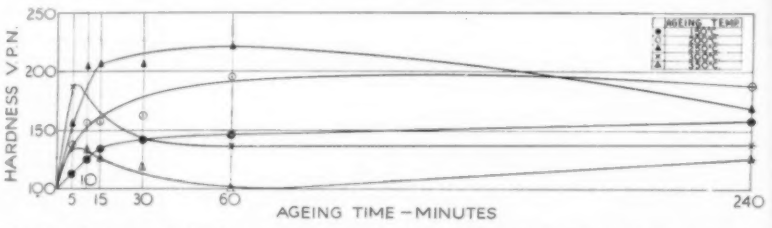


Fig. 9.—The precipitation-hardening of 1% aluminium sterling silver solution-treated for 3 hours at 770° C., and tempered at various temperatures.

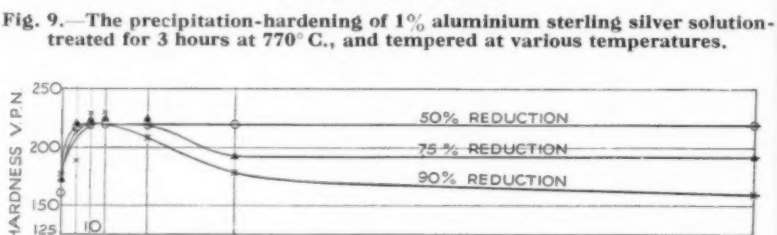


Fig. 10.—The precipitation-hardening of 1% aluminium sterling silver solution- treated for 3 hours at 770° C., cold rolled and tempered at 250° C.

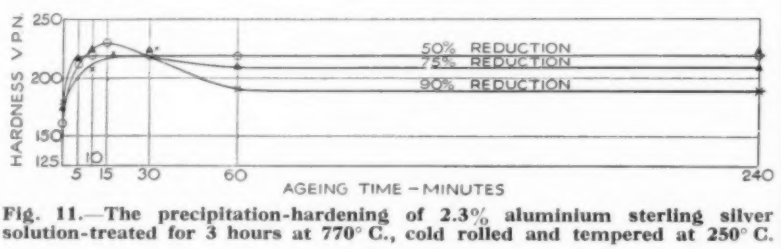


Fig. 11.—The precipitation-hardening of 2.3% aluminium sterling silver solution-treated for 3 hours at 770° C., cold rolled and tempered at 250° C.

Fig. 12.—Tea set and salver, in 1% aluminium sterling silver, designed and made by Mappin and Webb Ltd., Sheffield.

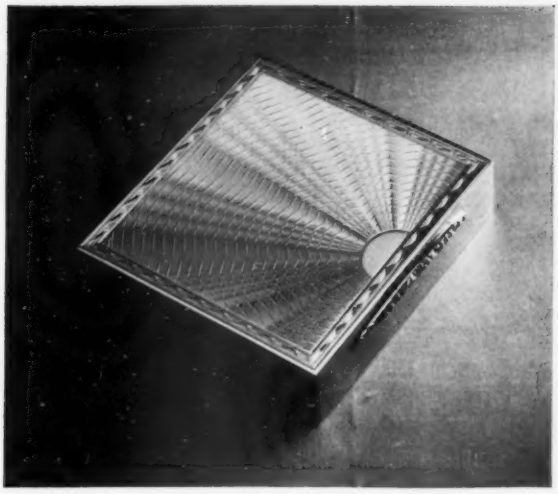


Fig. 13.—Cigarette box, in 1% aluminium sterling silver, designed and made by Mr. A. Morris, of Morris and Baker, Birmingham. Engine turning by Mr. H. Burr, of The Protos Co., Birmingham.

The comparative rate of annealing is shown in Fig. 8 to be similar to standard sterling, but the annealed alloy containing aluminium is always softer. As previously stated, grain growth occurs in standard sterling above 690° C., but not below 780° C. in the new alloy.

Thermal Hardening.—The comparative hardening obtained by reheating the solution-treated and quenched alloy is shown in Figs. 9, 10 and 11. The thermally hardened alloy is increased in tensile strength consistently with the hardness, but the elongation remains appreciable as shown in Table II.

Soldering.—The aluminium-bearing alloy is appreciably more difficult to wet with hard solder than is sterling silver, if borax only is used as a flux; nevertheless, skilled silversmiths have experienced no difficulty. The addition of 5–10% lithium fluoride to the flux removes the difficulty of wetting.

Ingot Casting.—Care is necessary in casting the aluminium-bearing sterling silver, as with all aluminium-containing non-ferrous alloys, to avoid entrapping oxide films in the ingot, but no serious difficulties have arisen. The cast ingot always has a bright and clean appearance, in contrast to standard sterling, which is usually discoloured with blue or coppery stains. In remelting scrap, the presence of aluminium can invariably be detected by skimming the surface and observing the instant formation of an alumina film in contrast to standard sterling which remains bright. Aluminium can be readily eliminated from a melt by melting under an oxidising flux such as manganese dioxide. The aluminium is oxidised first and its complete removal can be observed as above; if oxidation is further continued the copper also is oxidised.

TABLE II.—PRECIPITATION HARDENING OF ALUMINIUM CONTAINING STERLING SILVER.

Treatment	Hardness V.P.N.	U.T.S. Tons/sq. in.	Elongation %
Annealed	76	18·9	35
Solution treated, 30 mins. at 770° C. and quenched	80	20·1	40
Solution treated, 30 mins. at 770° C. Tempered 60 mins. at 200° C.	180	34·5	13
Solution treated, 30 mins. at 770° C. Tempered 15 mins. at 250° C.	206	37	13·5
Solution treated, 30 mins. at 770° C. Tempered 60 mins. at 250° C.	213	36·8	11·5

Tarnish Resistance.—The sterling silver containing 1% of aluminium is not less tarnish resistant than standard sterling under normal conditions, but Price and Thomas[6] have shown how a resistant but transparent alumina film can be developed on the alloy by suitable methods.

Density.—The density is about 2% less than standard sterling.

Craft Experience.—The above metallurgical data is of little value to the working silversmith who judges a metal entirely by its reactions to his skilled craftsmanship. For this reason many articles, varying from a complete tea set and salver to a cigarette case, have been made by experienced silversmiths and their comments reviewed. Briefly summarised these show that hand raising is slightly more difficult, but that spinning and hot forging are facilitated by the restriction of excessive grain growth; engine turning is unaffected. Soldering is somewhat more difficult and enamelling is so far, unsatisfactory. Polishing is affected because the alumina skin must be cut through by the abrasive, but is otherwise much facilitated by the absence of firestain. Most silversmiths consider the colour of the polished metal to be darker or slightly bluer than standard sterling, but this is not apparent to the uninitiated.

Acknowledgment

The Author wishes to thank the Council of the Design and Research Centre for the Gold, Silver and Jewellery Industries for permission to publish this paper, and also to Messrs. J. F. and R. Mills for the bulk of the experimental work.

1 E. A. Smith. *Nature*, 1937, **140**, 1,085.
2 *Mitt. forsch. Edelmetalle*, June, 1938.
3 British Patent No. 662,059 (1949).
4 J. L. Mayering and M. J. Druyvestyn. Phillips Research Reports No. 2, p. 262, August, 1947.
5 Anniversary Volume dedicated to M. Chijashiga, Kyoto Imperial University, 1930, p. 57.
6 *J. Inst. Metals*, 1938, **63**, 357–85.

Unorthodox Methods of Machining Hard Materials*

By P. Grodzinski, A.M.I.Mech.E.

The shaping of very hard materials, such as the sintered tungsten carbides, has given rise to a number of unorthodox machining methods, mainly of an electrical nature. In this article, the author reviews the present position, giving references to more detailed published information concerning the methods discussed.

CONSIDERABLE attention has been paid in recent years to methods of machining sintered carbides and other hard materials by processes which do not involve the use of abrasives, at least other than as a secondary material. These processes are of particular interest, as by their aid it is possible to produce complicated shapes with relative ease; they also permit the production of smooth surfaces of greater endurance. Such methods have been developed mainly in Russia, America and Germany.

Oxidation

In 1931, Fehse[1] suggested the oxidation of hard metal plates as a means of reducing their dimensions whilst maintaining the geometrical shape. Where protection from oxidation was desired on any particular face, this could be achieved by the application of a layer of copper. Ballhausen[2] smoothed the cutting edges of hard metal tools by subjecting them to the following oxidation treatment: the tool tips were ground in the usual way and then oxidised at 800° C. by furnace heating or by heating with an oxidising gas flame, instead of lapping and polishing. It is stated that tool edges with very small cutting angles can be obtained, such as are used for cutting paper and textiles. Wire drawing dies, press tools and hard facings may be similarly treated. In some of the electrical methods described later, oxidation is probably a factor in the mechanism, but this will be treated separately.

Chemical Action

Chemical treatments such as are occasionally used for sharpening steel files are not possible with sintered carbides, as in this case the metallic binder (i.e., cobalt) is preferentially dissolved. Dawihl and Hinnüber[3] have shown that after treatment in acids for 24 hours the whole of the cobalt is dissolved and only the tungsten carbide skeleton remains. If the surface is attacked by acids at the same time as it is rubbed slowly by a disc, the exposed carbide particles are removed. Since operation with acids has many disadvantages, a solution of copper sulphate has been suggested by some Russian workers[4]. The cobalt is then dissolved by exchange with copper and protection of other surfaces is readily achieved. Arrangements similar to the usual disc lapping machine have been described in Russian publications. The hard metal plates are lapped on two opposite faces between slowly rotating discs of copper or stainless steel. The fluid is a 20–25% copper sulphate solution in which is suspended fine emery powder. The compound should always contain free copper sulphate.

Electro-Mechanical Methods (Low Voltage)[4a]

If two metals are held in frictional contact, with an electric current passing from one to the other, the metal forming the anode will be rapidly destroyed even if very light pressure is applied, whilst destruction of the metal forming the cathode is insignificant. A number of methods using this principle have been described, some working in air and some in a liquid medium.

At the Hanover Industrial Fair, 1951, Naxos Union[5] showed an electrical lapping machine for sintered carbide tools, in which a small electric arc was created between the rotating steel disc and the fixed sintered carbide tool edge; no coolant was used.

The method of cutting metals dry (i.e., in air) by an electric current was suggested by Orlov[6] in 1935, but at an earlier date (1929) W. Gusseff[7]† suggested an electrolytic process, whilst in later literature on methods using electrical means the use of gases and air is frequently suggested as an alternative. W. Gusseff[7] used electrolytes such as 3–8% hydrochloric acid circulating continuously. The action is said to depend on the speed, which is, for preference, 300–600 metres per minute, the voltage being 110 and the current density 50–300 amps/sq. cm. The method further depends on the material of the tool cathode being mounted inside an insulating shield, and the workpiece used is the anode.

Orlov[6], in 1935, suggested a method of cutting metals using 3-phase alternating current. This was applied to the workpiece to be machined and two discs acting as tools, the current intensity being of the order of 10,000–20,000 amps at 5–10 volts; the cutting operation was carried out in air. Obvious defects of this method, mentioned in British Patent 637793, include the high temperatures generated by eddy currents.

These high temperatures are said to have been avoided by Lazarenko and Lazarenko[8] by a spark discharge, using direct current of the order of 8 amps at 150 volts with a condenser of about 200 microfarads to cause an oscillatory discharge. A liquid medium (dielectric) such as kerosene, prevents the material to be removed from the anode (workpiece) from being deposited on the cathode (tool) and thus changing its form. Drilling, turning, grinding, sawing and engraving operations are said to be possible. Sometimes the tool also appears to be used as the anode. The same workers have also obtained patents for a similar method for

* Partly according to C. Ballhausen, "Bearbeitung von Hartmetall-legierungen ohne Schleifen" ("Machining of hard metal alloys without grinding") *Stahl und Eisen*, 71, 1951, 1,114, 1,115.

† As spelt in his British Patent; V. W. Gusev in Russian literature.

producing powders[9] and for recording metallic corrosion[10].

After these historical notes, we may now turn to some recent publications in the technical press. Popilov[11], with a disc rotating at a speed of 2,400–3,600 feet per minute (12–18 metres per second) and a D.C. current of 20–100 amps at 22–24 volts, uses as lubricant commercial waterglass with the ratio $SiO_2 : Na_2O = 2$ to 3 : 1, or even clay. Ulitin[12] uses similar speeds, but voltages of 20–220 and D.C. currents from 1–150 amps, the capacity of the oscillator circuit being 1–400 microfarads. The material of the disc is cast iron, steel, cupro-graphite or aluminium, and the author investigated various conditions, obtaining optimum values from 20–25 volts.

Nevezkin[13] has investigated the operation of a circular saw, using direct current of 200 amps at 6 volts. The cathode is disc shaped (170 mm. diameter, 920 r.p.m.) and an impulse discharge occurs between the electrodes. The measurement of the minimum voltage at which discharge is set up in air, water, aqueous solutions of salts, and oils, shows that at voltages of 11–13, and at a sufficiently small electrode spacing, the discharge is of the contact-less type. If the circular saw spark operates at tensions below 11–13 volts, periodical opening and closing of the electrodes occurs and contact breaking results in production of over-voltages of 12–15 volts at which an impulse discharge occurs lasting about 10^{-4} seconds. An empirical formula can be obtained for the relationship between the voltage across the electrodes and the discharge current in air and aqueous solutions of salts (i.e., $V = 12 + 0{\cdot}63I^{\frac{1}{2}}$).

Muravchik[14] has applied an improved Gusseff[7] method successfully to the sharpening of sintered carbide drill bits, whilst Noskov[15] and Ulitskii[16] report on results obtained in tool grinding.

Rudorff[17] (London) obtained patents (applied April to October, 1947) for a method of removing the material from electrically conducting materials in which, between the electrode acting as tool and the material to be machined, preferably sintered carbides, etc., an electric spark is used in the presence of an uninterrupted flow of liquid which acts as a coolant and prevents an uninterrupted arc. Recommended fluids include electrolytes such as water glass solution, phosphoric acid solution, boric acid solution, a mixture of several electrolytes, or a dielectric fluid such as oil; a gas consisting of at least two chemical elements can also be used. In this method, the tool electrode acts as cathode and the workpiece as anode, direct current at a voltage between 20 and 200 being used with self induction. The specification describes the application of the method for a number of machining operations such as sawing, turning, etc. The main difference between the Lazarenko and Rudorff patents is that the latter uses a unidirectional current, and through this the wear of the electrode is considerably reduced and a higher surface finish obtained. Recently, Sparcatron, Ltd., has been formed in Gloucester to exploit the Rudorff and similar patents[17a]. Two disintegrating devices of this firm were exhibited at the recent London International Machine Tool Exhibition, September 1952.

A sensitive electrically controlled device provides the feed of the tool electrode towards the workpiece. The unit is relatively small and may be attached to any type of machine. The negative tool electrode is fixed in a chuck on a vertical holder, which is moved by a servomotor through a rack and pinion. The workpiece clamped to the machine table is situated in a bath of dielectric fluid. Piping from the bath leads to a sump and filter from which the fluid is pumped back to chuck and electrode. A signal voltage proportional to the discharge current is fed from a resistor in series with the electrode and combined with a reference voltage. It is so adjusted that the effective signal voltage in the system is zero when the electrode member is in the correct position relative to the work. Should the electrode change this position—perhaps due to wear—a positive or negative signal is fed into the amplifier, the output of which energises a D.C. motor, which operates the rack and pinion movement.

In this connection it may be noted that the so-called Elox method developed in 1943 for the removal of broken taps and drills has now been developed as a general arc-machining method[18], on similar lines to the above. D.C. current is used with the tool as cathode and the workpiece as anode, the tool itself being either copper or molybdenum. The latter is better for high temperature applications, but the high price limits its use. The most important factor is the fluid used, water and soluble oil compounds being recommended for rough machining, whilst for fine precision machining operations dielectric cooling media which do not allow of electrolysis are said to be better. According to the type of work, the fluid is used at a pressure in the range 40–400 lb./sq. in., an average figure being 120 lb./sq. in. The fluid can be fed to the work: (*a*) down through the hollow electrode; (*b*) up from the bottom of the work through a previously drilled hole; or (*c*) from the side through slip fittings. The following data of stock removal in cubic inch per minute to give a 60 micro-in. r.m.s. finish are quoted: die cast zinc alloys—0·200; steel and steel alloys regardless of hardness—0·025; nickel and nickel alloys regardless of hardness—0·050; tungsten carbide—0·004; and titanium carbides—0·020. The rate of stock removal is, of course, reduced when fine finishes are produced. The latest developments include the production of good surfaces and sharp cutting edges on sintered carbide tool bits, but field tests have not yet been made with tools sharpened in this way. It is considered that future developments may diminish the heavy demands made on diamond grinding wheel equipment. This method was demonstrated by Marbaix at the recent International Machine Tool Exhibition, London.

The methods developed by Lazarenko and Vasiliev have been investigated with regard to their electrical and mechanical details by Koncz[19] at the Mechanical Technological Institute of the Technical University, Budapest; in particular, the current characteristics were investigated by means of oscillographs. The following conclusions were reached: (1) The material removed from the component is proportional to the power taken from the condenser: the specified loss values in cubic inch $\times 10^{-9}$/Joule are: mild steel—111, cast iron—73, Widia—98, copper—195, and aluminium—348; (2) the loss per discharge curves become straight lines above 100 volts; (3) the arc which may follow the discharge process is supplied by the direct current source: it should be suppressed as it decreases the efficiency of spark machining; (4) spark machining probably consists in the heating of the material at the point of contact to a temperature above its boiling point, followed by sudden disintegration: the subsequently formed arc does not increase the loss of

material; (5) spark machining is not economical when compared with the usual methods of machining medium-hard metals, but it is advantageous both from an economic standpoint and as regards quality of machining on very hard metals, and it is the only possible method, apart from diamond grinding, for the hardest metals; (6) the efficiency of spark machining is constant above 100 volts; (7) the quality of drilled holes increases if the material loss/discharge decreases; (8) by using an oscillating charging circuit the voltage of the D.C. generator can be lowered by nearly 50%, thus increasing the safety of the personnel.

Electro-Mechanical Methods (High Voltage)[19a]

Some of the difficulties in the methods described above, in particular the control of the arc condensers, are said to be avoided with the American electro-mechanical Method X which uses high frequency current for producing holes or shaped forms in dies[20]. The machine is similar to a drilling machine with a feed arrangement which in this case operates the electrodes, control devices and adjustments, together with the adjusting device for the workpiece. The coolant container is set up on the table of the machine, the insulating fluid being oil; a special fluid (not described in detail) is said to promote uniformity and to disperse the spark arc discharges. Appreciable evaporation of the fluid takes place and a special suction device is provided for its removal. The electrodes are of copper and any desired cross-section can be used. As they do not come into contact with the material, no contact pressure is necessary. The high frequency A.C. current is produced by a valve generator and can be accurately controlled, in contrast with D.C. arc discharges which can only be controlled by condensers and induction coils. The Method X can be used for such operations as drilling, trepanning, broaching, shaping and engraving of hard metals and other alloys. Particular reference is made to the accurate machining of turbine blades, and allowance of only 0·002 to 0·004 mm. being necessary for producing smooth surfaces; no greater deviation than 0·01 mm. need occur.

Electric Grinding with Metal-Bonded Diamond Grinding Wheels

A promising new method has been developed by Keeleric of United Drill and Tool Company[21]; it is an electrolytic grinding operation which differs from the spark and arc methods already described. Both the Elox[18] and Method X[20] techniques cause small particles of tungsten carbide to be dislodged mechanically from the main workpiece. This occurs when the spark or arc is exploded between the work and the electrode. In the electrolytic method, stock removal results from a chemical decomposition of the material to be ground.

Keeleric's method uses a metal-bonded diamond grinding wheel together with D.C.-electric current of about 80 amps (depending on the area of contact) at 18 volts. Existing grinding machines can easily be converted for use with this method as it is only necessary to insulate the diamond wheel from the rest of the machine by a fibre disc mounted between the wheel and the adaptor. Brushes are mounted behind the diamond wheel and baffle plates are used to keep them dry during the operation of the machine. The positive pole of a rectifier is connected to the earthed table on which the tool rests and the negative pole is connected to the brushes behind and in contact with the diamond wheel. As the wheel rotates, an electrolyte floods the top of the tool, forming a film of fluid between the tool and wheel. The tool is firmly fixed to the table and current passes from the table to the tool, through the film of electrolyte to the metal bond of the wheel, and back to the rectifier. The diamonds in the wheel perform two functions: they space the tool from the wheel and at the same time prevent an oxide film being formed. When the tool is less than 0·0007 in. from the wheel, an arc or spark occurs which is injurious to both the wheel and the tool. The diamond grains protruding from the surface of the wheel should project sufficiently to give a greater clearance than the figure quoted, and so permit the electrolyte to flow between the tool and the matrix of the wheel. As the operation proceeds, a film of tungsten oxide is formed on the face of the tool against the wheel, but diamond grains continually wipe this film away and thus permit constant electrical or chemical action. The metal from the tool face contacting the wheel is rapidly dissolved and carried away as tungsten oxide which is found in the electrolyte, instead of the tungsten carbide of the spark and arc methods. In this process the insulating properties of diamonds are utilised.

Without any pressure of the tool against the wheel, metal is removed relatively quickly, and investigations are now being carried out to make comparisons with conventional diamond grinding. The first manual test established the same rate of stock removal and it is expected that the absence of pressure between the wheel and the tool will considerably increase the life of the metal-bonded diamond wheel. When pressure is used with the new electrolytic method, a combination of electrolytic grinding and diamond grinding is obtained, and the grinding rate is four times as quick as it is without pressure. However, the corresponding tests have not yet been completed.

The electrolytic action applies, without loading the wheel, to the steel shank as well as to the sintered carbide, and the grinding speed is so high that a preliminary grinding or relieving of the steel shank below the carbide tip seems to be unnecessary. With conventional diamond grinding, the larger the area of contact between the carbide and the steel face, the slower the grinding, but in the electrolytic method the larger area of contact causes higher amperage to be used and the same thickness of layer, i.e. amount of material is removed. The new method produces a different type of finish, and surface finishes ranging from 5–14 micro-in. r.m.s. have been produced; these are well within the range of satisfactory surfaces for sintered carbide grinding. No change in technique is required and no heat of any kind is generated in electrolytic grinding—in fact, it may be considered as one of the coolest processes for machining carbides. The composition of the carbide is not affected and fissures and cracks are not produced.

Keeleric and Metzger presented a paper on the development of electrolytic grinding to the American Society of Tool Engineers. One of the main items of the equipment is a special rectifier, which controls automatically the output voltage. If, for a given spacing between wheel and workpiece, too high a D.C. voltage is delivered, sparks will occur between them. Sparks are to be avoided as they tend to erode the workpiece and wheel electrode; in particular, they reduce the surface finish and, in form grinding, the accuracy. The unit auto-

matically lowers the voltage as soon as excessive or hot sparking occurs. The price of such a rectifier is estimated at $1,800 to $2,000. The electrolyte is relatively inexpensive: hitherto solutions of highly conductive sodium salts were used, which work reasonably well, but further investigations are under way. Originally, aluminium oxide and silicon carbide grinding wheels were investigated but they proved unsatisfactory. The diamond wheels now used have a higher diamond concentration and, according to the Keeleric patents, only a single layer of diamond is applied. Even with a higher concentration than 100 (according to present American usage 100 concentration corresponds to diamond contents of 72 ct/cub. in.), the price of these wheels will be much lower than that of standard sintered wheels. The face of the wheels must run extremely true and the wheel flanges are provided with tension and compression bolts to fix them evenly.

Electric Spark Toughening

Other Russian authors have described another method[22] which they call "electric spark toughening," in which a non-rotary electrode is held by hand against the tool edge. Electrical discharge takes place between a suitably chosen electrode material and the surface to be treated, microscopic particles of the electrode material being transferred to the tool surface, penetrating into it and, allegedly, hardening or toughening it. For instance carbide particles are produced in the tool surface when a graphitic carbon electrode is used. This operation takes place in air and no particular lubricant is used.

Ultrasonic Method

A purely mechanical machining operation exploiting the cavitation due to ultrasonic vibrations[23] is the American Cavitron method. A steel bar is held at a small distance from the plate to be trepanned, and under ultrasonic vibrations the form of the tool is reproduced in the plate; a stream of water containing an abrasive, preferably boron carbide, flows between vibrating tool and work.

Sudden Changes in Temperature

The high degree of sensitivity of sintered carbides to sudden changes in temperature has also been exploited. When using one of the electrical writing instruments on sintered carbide plates, the plates break exactly along the lines engraved. It is, therefore, a general rule that such plates or tips should not be marked electrically. Further, it has been observed that sintered carbide plates break immediately when they are brought between the electrodes of an electric spot welder, and when guiding the flame of a cutting torch over a cold sintered carbide plate, shell-like pieces are broken out. These phenomena have been ingeniously exploited in the Thomas Metalmaster, 1950[24], in which an A.C. spark of about 135 amps, 3–15 volts, is formed between the sintered carbide plate and a hollow electrode. At the same time, coolant under pressure, supplied through the electrode, immediately quenches the spark. As a result of the high and suddenly generated heat stresses, small shell-like particles break away from the attacked surface and with a correspondingly adjusted feed and controlled coolant, holes can be made in a surprisingly short time. For instance, ¼ in. thick sintered carbide plates can be penetrated in 5 minutes, and cylindrical holes from 0·04 in. to 2 in. in diameter can be made, as well as holes of arbitrary shape. The coolant is not described but is apparently not electrically conductive.

Conclusion

This short survey of the literature, which could be considerably extended[25], has shown that there are a number of unorthodox methods of machining and that these can be applied to a number of different operations such as drilling, sawing, grinding, polishing of cutting edges, trepanning of arbitrary forms and even of bent holes[26]. Similar methods to those described for conductive materials have been developed for non-conductive dielectric materials such as diamonds[27], and it cannot be ruled out that the mechanism of the electrical method has not been fully understood, as similar results may be obtained by ultrasonic vibrations and the application of local heating. It would be a most useful undertaking if the mechanism of these processes could be clarified by a more detailed study.

The various methods discussed have recently been critically surveyed in America by the Minerals and Metals Advisory Board of the U.S. Nat. Res. Council[28]. Table I shows how 8 important machining and grinding operations commonly using diamond abrasive can be performed by these processes. The report concludes, however, that none of the new processes is in actual commercial use except for shaping and finishing dies.

Whilst, in general, emphasis is laid on the development and improvement of the processes from a practical point of view, some theories of the mechanism of the electrical spark and arc methods have been advanced. Lazarenko has suggested 'electrolytic' action and 'electrodynamic' forces. Other Russian workers explain that the erosion may be due to the explosive force of the discharge, increased by a high-temperature metal-vapour flare propagated from the cathode (electrode) towards the anode (workpiece). Rudorff suggested that oscillating mechanical forces, similar to those in cavitation are involved. Williams[29] finds that these theories are only qualitative, and shows that the phenomenon of breaking

TABLE I.—IMPORTANT MACHINING AND GRINDING OPERATIONS AND ESTIMATED APPLICABILITY OF METHODS

Job item or operation	Applicability of methods					
	Percent use of diamond boart*	Diamond wheel grinding	Electrolytic	Electro-sparking†	Electro-arcing‡	Ultrasonic
Sharpening of single-point tools	30	A	B	B§	C	B§
Grinding single-point tool chip breakers	20	A	B	B	C	B
Sharpening milling cutters and broaches	15	A	B	B	C	B
Grinding projectile cores	5	A	B	B	C	B
Shaping and finishing dies	4	A	D	A	D	A
Forming turbine-bucket attachments	—	B	B	B	C	B
Rifling gun barrels	—	B	C	B	C	B
Machining and grinding compressor discs	—	B	B	B	C	B

A—In use on production scale.
B—Appears applicable; promising but limited experimental data to date.
C—Questionable applicability; not promising but might be developed to be promising.
D—Limited applicability or not applicable; not usable in present state of development.

* Approximate percentage of total diamond boart currently being consumed in U.S.A. All diamond wheel grinding consumes about 85% of boart and operations considered account for 75%. Remaining 10% is used for a multiplicity of operations.
† Described here as: Electro-mechanical method (high voltage) see p. 36.
‡ Described here as: Electro-mechanical method (low voltage) see p. 34.
§ Not applicable for off-hand grinding, but appears applicable for machine grinding.

up material can be explained by the erosion due to electric field forces. In a particular instance he shows that at a bottom of a fragment a stress of 145,000 lb./sq. in. may be acting (neglecting shear stresses) which is higher than the breaking strength of the material and may account for the fracture.

REFERENCES

1 German Pat. 564 081 (15th March, 1931).
2 German Pat. Appl. 48d, 5 D352 (31st July, 1943).
3 *Kolloid Zeits*, **104**, 1943, 233–236.
4 Z. I. Shulvug, *Stanki I Instrument*, **15**, 1944, 26–27; translated in *Ind. Diamond Rev.*, **5**, 1945, 148, and *Machinist*, **90**, 1946, 540. B. S. Korshunov, S. P. Mogurova in their text book "Sharpening and Finishing of Hardmetal Tools," Moscow, 1951. E. Ya Ulitskii, *Vestni Mashinostro*, **3**, 1949, 47–55.
4aIn America named: electro-arcing.
5 *Ind. Diamond Rev.*, **11**, 1051, 201.
6 Russ. Pat. 45 017 (1935).
7 Brit. Pat. 335 003 (24th July, 1929), there is also a Russian Pat. 34 253 of V. N. Gusev (20th June, 1931).
8 B. R. Lazarenko, N. J. Lazarenko, Brit. Pat. 637 793 (24th September, 1946).
9 B. R. Lazarenko, N. Y. Lazarenko, Brit. Pat. 627 713 (24th September, 1946).
10 B. R. Lazarenko, N. I. Lazarenko, V. R. Lazarenko, Russ. Pat. 64 705 (31st December, 1943).
11 L. Y. Popilov, *Zavodskaya Laboratoria*, **14**, 1948 (3), 358–361.
12 M. N. Ulitin, *Stanki I Instrument*, **21**, 1950, (10), 3–6 (detailed investigation, cutting speeds, surface finish, etc. apparently using the Lazarenko method—see footnote 8). Engl. translation in *Machinery* (Lond.), **90**, 1952, pp. 760–764.
13 V. K. Nevezkin, *Elektricheatro*, 1951, (11), 62–70.
14 L. V. Muravchik, *Gornyi Zhurnal*, 1949, (5), 25–27.
15 S. E. Noskov, *Stanki I Instrument*, **19**, 1948, (10), 20–22.
16 T. P. Rekshinskaya Automobilnaya Promishlenost 1946, June 5th, 12–15, mentioned by L. Guimin, *Machines et Metaux*, **32**, 1948, 81–82. *Engineers' Digest*, **8**, 1947, 216–217. E. Ya Ulitskii, *Vestn. Mashinostro*, **3**, 1949, 47–55, *Bibl. Ind. Diamond. Appl.*, **6**, 1949, 497.
17 Brit. Pat. 637,872. Swiss Pat. 273,469 (Convention date Gt. Britain, 10th April, 7th July and 24th October, 1947).
D. W. Rudorff has also given a survey of the development of the electric fragmentation process (*Engs. Digest*, **10**, 1948, 306–308). According to this the first experiments with this method were carried out by G. Bredig in 1898 for the production of colloidal metals. He further draws attention to a German war-time patent (no further information given) for metal cutting by ultrasonic vibration of the order of one hundred thousand to one million cycles per second (see section ultrasonic method).
17aM. G. Seed, Britain, too, is developing electro-spark machining, *Machinist*, **90**, 1952, pp. 977–981, and other Brit. periodicals.
18 H. V. Harding, V. E. Matulaitis, *Am. Machinist*, **96**, 1952, 136–141 (March 3rd). It is referred to the following U.S. Patent Specifications:—
2 374 348, H. V. Harding (2nd October, 1943) Chuck and electrode.
2 383 383, H. V. Harding (14th October, 1943), Electromagnetic vibratory metal working apparatus.
2 415 690, A. A. Holfelder (1st May, 1943), Method of and means for removing embedded material.
2 427 588, H. Y. Burnett (17th October, 1942). Apparatus for boring holes in metal.
2 441 319, H. V. Harding (2nd October, 1943). Disintegrating or removing metallic material (mechanical vibrating electrode).
2 501 954, J. C. McKechnie, Roy E. Blue, Lester E. Oliphant, (28th June, 1945). Electric arc drill.
Some of the quoted Patent specifications contain references to similar older specifications and literature.
Equivalent Brit. Patentsare: Brit. Pat. 610 709 (convention date U.S.A. Oct. 2, 1943), 588 659 (convention date U.S.A. July 19, 1943) and 578 933 convention date U.S.A. July 19, 1963).
It is also mentioned that one of the machines was sold in 1945 to the Russian Purchasing Commission and that the data obtained undoubtedly started the Russian development of arc machining processes. This, however, seems to be incorrect as Russian and other patents by V. W. Gusseff date from 1929.
19 I. Koncz, *Gep.* (Hungary), **1**, 1949, 388–411. *Engineers' Digest*, **11**, 1950, 108–111, 165–168.
19aIn America named electro-sparking. *Steel*, **130**, 1952, pp. 84–86 (Mar. 17).
20 J. S. Roller, Method X Co., Phil. *Machinery* (N.Y.), **58**, 1951, 180–181; M. F. Judkins, D. F. Dickey, *Iron Age*, **168**, 1951, 65–67 (July 26th); *Bibl. Ind. Diamond Appl.*, **8**, 1951, 658; *Am. Machinist*, **95**, 1951, 172–190 (only even Nos.), 191, 193, 194–216 (only even Nos.) (March 5th), abstracted *Ind. Diamond Review*, 1952, **12**, pp. 70–72 (March).
21 *Iron Age*, **169**, 1952, 203–207 (March 6th) and according to a paper of G. Keelerie and L. H. Metzger presented Oct. 2, 1952 to American Society of Tool Engineers.
22 S. Va Bazarov, A. A. Biryukov, *Sels 'Khosmachina*, No. 3, 1951, 29–31 (March).
B. Maczewski-Rowinski, *Przeglad Techniczny*, No. 6, 1951, 277–280.
23 S. G. Kelley, Jun., *Materials and Methods*, **34**, 1951, 92–94 (September); *Engs. Digest*, **12**, 1951, 373, see also footnotes 17 and 18. A. Kuris, *Machinery (Lond.)*, **79**, 1951, 991–992. See also L. Balamuth, U.S. Pat. 2 580–716, (Jan. 11, 1951) suggesting vibrations between 400 to 1,000,000 cycles per second of an amplitude not more than 0·05 in. in a liquid containing an abrasive.
24 Clinton Machine Co., Clinton, Mich., U.S.A.
25 G. P. Ivanov, *Stanki I Instrument*, **22**, 1951, 20–22. L. Kocsis, *Magyar Techn.*, 1950, 7–10 (July).
26 V. I. Kurchenko, *Stanki I Instr.*, **22**, 1951, 34 (June).
27 See U.S. Pat. 2 438 941, C. G. Peters and coll.
C. S. Peters, K. F. Neffien, F. K. Harris, *Journ. Research Nat. Bur. Standards*, **34**, 1945, 581–593, abstr. *Ind. Diamond Rev.*, **5**, 1945, 288–291.
28 Report M.A.B. 18–M. extract in *Am. Machinist*, **96**, 1952, pp. 130–131 (Mar. 17).
29 E. M. Williams, Theory of Electric Spark Machining, *Elec. Eng.*, 1952, **71** 257–260, March.

Automatic Control of Open Hearth Furnaces

Continued from page 26

below stage level, the values being transmitted electrically to the control cubicle to operate flow indicators and flow recorders.

Control Oil Pumps.—All the controllers are of the Tinsley/Askania vertical-jet-pipe type, and are operated by oil pressure. The oil is supplied by a double-helical gear pump and a stand-by oil pump is provided in case of failure of the main oil pumps. On such a failure, the control oil pressure will fall slowly and the stand-by pump will be started automatically. The hydraulic circuits for the automatic reversal unit are supplied by a separate oil pump, and here again a stand-by pump is provided which starts automatically on failure of the main pumps. Warning lights are provided on the control desk to indicate to the furnace operator any failure of control-oil or reversal-oil pressure.

New Training Scheme for Foremen

Mr. H. Humphries, Deputy-Chairman and Managing Director of Hadfields, Ltd., has announced that the company is introducing a new scheme for the further intensive training of foremen. Tuition will be given on such subjects as work study, productivity, quality control, the conservation of man-power, materials and machine tools. The further object of this innovation is to make the foremen more familiar with the overall activities of the company, and of departments other than those which they themselves control.

The participants will attend residential courses at the Hecla Works, commencing on Monday, 12th January, 1953, and will later attend a continuation course at the company's East Hecla Works. Local directors and other senior officials of the company will give the lectures, and time has been set aside for discussions and visits to operating departments.

The inauguration of this scheme marks a further step in the training of employees of Hadfields, Ltd. Already more than 100 apprentices are being trained under the guidance of a training officer and other skilled instructors, with the object of increasing their proficiency in the craft, technical and commercial sections of an establishment whose main concern is the manufacture of high quality steels and heavy engineering.

All-Basic Open-Hearth Conference Report

The report of the All-Basic Open-Hearth Conference held in Glasgow in June, 1952, is now published at 7s. 6d. It contains the full text of the papers by Mr. Mitton and Mr. van Stein Callenfels and the abstract paper by Mr. Mackenzie, together with the complete discussion. Copies may be obtained from the West of Scotland Iron and Steel Institute, 39, Elmbank Crescent, Glasgow, C.2.

NEWS AND ANNOUNCEMENTS

The Institution of Metallurgists

H.R.H. The Duke of Edinburgh

THE Council of the Institution of Metallurgists have great pleasure in announcing that His Royal Highness, The Duke of Edinburgh, has graciously accepted election to Honorary Membership of the Institution.

B.W.R.A. Summer School of Welding

THE third Summer School of Welding organised by the British Welding Research Association will be held at Ashorne Hill, near Leamington Spa, from Monday, April 27th, until Saturday, May 2nd, 1953.

This year, the general theme of the School is welding fabrication and production and the various aspects will be covered in logical sequence during the course. The School will start with introductory lectures giving critical and comparative studies of welding processes, plant, and basic materials. Students will then be given full instruction in welding design followed by lectures on study of works planning and welding costs and the more efficient use of up-to-date processes such as automatic welding, etc. Finally, the use of standardisation, time and motion study and other means of improving productivity will be given. The course will also include lectures on the non-destructive testing and inspection of welds and others of special interest.

To assist industrial organisations whose staff may be more particularly interested in one aspect of welding, the School has been divided into certain groups. Students will be given lectures of general interest usually in the morning, followed in the afternoon by lectures on more specialised subjects under five group headings :—

Group A : Aircraft Industry ;
Group B : Shipbuilding Industry ;
Group C : Structural Engineering ;
Group D : Automobile and Sheet Metal Industries ;
Group E : General Engineering.

The School will be of great use to designers, technicians, engineers and, indeed, all those interested in improving welding methods and production efficiency. As vacancies are limited, it is suggested that those wishing to attend the School, or send representatives from their organisations, should communicate as soon as possible with the Secretary, B.W.R.A. Summer School of Welding, British Welding Research Association, 29, Park Crescent, London, W.1, requesting the necessary application forms and full particulars.

The Institution of Metallurgists

Examinations, 1952

The following candidates have been successful in the Institution's Examinations :

Associateship : J. G. Beynon (New Maldon) ; D. Boxall (Windsor) ; G. B. Clarke (Enfield) ; L. H. Cope (Kettering) ; J. K. Critchley (Sidcup) ; F. M. Davis (Jarrow) ; M. Donovan (London, W.14) ; E. G. Hall (Aldermaston) ; H. C. Hardwick (London, W.14) ; J. R. V. Harvey (Leyton, E.10) ; J. A. N. Lawrie (New South Wales) ; W. H. C. Parker (Glasgow) ; M. D. Payne (Leamington Spa) ; J. W. Rowley (Birmingham) ; G. E. Spriggs (Coventry) ; M. Stevens (Lytham-St. Annes) ; R. A. Storer (Birmingham) ; K. G. Sumner (Sutton Coldfield) ; P. C. Thornton (Romford) ; S. R. Twigg (Stoke on Trent) ; W. R. Utteridge (Peterborough) ; H. H. Vevers (Slough) ; T. D. Weaver (Bristol) ; and D. White (Atherstone).

Licentiateship : K. Aldersley (Huddersfield) ; C. J. Barfield (Hatfield) ; A. J. D. Binstead (Bedford) ; R. V. Blewett (Beaconsfield) ; A. M. Bowen (Birmingham) ; J. H. Ellis (Kettering) ; J. P. Evans (West Croydon) ; A. G. Ford (Coventry) ; F. A. Green (London, N.4) ; H. C. Hardwick (London, W.14) ; M. A. H. Howes (Birmingham) ; B. J. Jones (Llansamlet) ; D. Jones (Port Talbot) ; G. R. Kirkland (Manchester) ; D. Lewis (Dudley) ; G. I. Lewis (Potters Bar) ; D. E. MacQuarrie (Wembley) ; D. E. Mansfield (Wandsworth) ; E. L. Morgan (Corby) ; C. G. Odell (Tibshelf) ; D. J. Pucknell (Cleethorpes) ; R. T. Saxon (Liverpool) ; D. Sen Gupta (Muradnagar, India) ; B. F. Sharpe (Streatham) ; H. Spankhurst Smith (Bexleyheath) ; D. A. Spooner (N. Wembley) ; P. B. Swift (Coventry) ; D. W. Trotman (Bristol) ; F. J. Turner (Birmingham) ; S. R. Twigg (Stoke-on-Trent) ; R. G. Ubank (Bristol) ; T. D. Ward (Birmingham) ; and E. Joseph Williams (Merstham).

The next Examinations will take place August 24th—September 1st, 1953, and copies of past examination papers, together with Examiners' Reports are available at 1s. per set.

The Institute of Metals

Medal Awards for 1953

THE Council of the Institute of Metals has made the following awards of medals for 1953 :

The Institute of Metals (Platinum) Medal : To Professor GEORG MASING, of the Institut für Allgemeine Metallkunde, Universitat Göttingen, in recognition of his outstanding contributions in the field of metallography.

The Rosenhain Medal : To Dr. C. E. Ransley, of the Research Laboratories, The British Aluminium Co., Ltd., Gerrards Cross, in recognition of his outstanding experimental and theoretical work on gas-metal equilibria.

I.M.F. Organic Finishing Group

THE inaugural meeting of the newly-formed Organic Finishing Group of the Institute of Metal Finishing will be held at the Charing Cross Hotel, London, on Thursday, 19th March, 1953. The programme for this first meeting includes lunch, inaugural meeting, and two technical papers followed by discussion, with a break for afternoon tea. At the meeting, the committee which will be in charge of the Group's activities for the following year will be elected. This Committee is to consist of eight officers, in addition to the President and Hon. Secretary, who will be *ex-officio* members.

In order to extend the scope of the Group's work, nominations to this Committee are invited from interested parties : the nominees need not, necessarily, be members of the Institute of Metal Finishing but will,

of course, be expected to become members in the event of election. Each nominee must be nominated by two persons whose names, business address and status should be given on the nomination form. This form is obtainable from the Head Offices of the Institute, 32, Great Ormond Street, London, W.C.1, and must be returned not later than March 1st.

The meeting will be open to all interested, whether I.M.F. members or not, and further details of the authors and subjects of the technical papers will be given later.

Mond Nickel Fellowships

1952 Awards

THE Mond Nickel Fellowships Committee announces the following awards for 1952 :—

MR. A. G. DUCE (Joseph Lucas (Gas Turbine Equipment), Ltd., Burnley) to study in the United Kingdom, on the Continent, and in the U.S.A. and Canada, the metallurgy and testing of materials, especially in sheet form, developed for high temperature service, and the techniques employed in the manufacture of the combustion systems of gas turbine engines.

MR. F. G. HORTON (National Foundry College, Wolverhampton) to study casting production methods in the United Kingdom and on the Continent, with special reference to shell moulding, centrifugal casting, and sand-cement moulding.

MR. H. A. LONGDEN (Steel, Peech and Tozer, Ltd., Sheffield) to study metallurgical control methods in the United Kingdom, on the Continent, and in the U.S.A. and Canada, with special reference to open-hearth slag and temperature control.

MR. G. P. KEMPSON (Henry Wiggin & Co., Ltd., Birmingham) to study the development, application and control of ferrous and non-ferrous melting and ingot casting processes in the United Kingdom, on the Continent, and in the U.S.A. and Canada.

Distribution of Primary Nickel

The Manganese-Nickel-Cobalt Committee of the International Materials Conference announced recently that its 14 member Governments had accepted a first quarter 1953 distribution plan for primary Nickel and Oxides. The recommended plan of distribution has been forwarded to all interested Governments for implementation.

As in the distribution plans for the last two quarters of 1952, provision has been made whereby any nickel allocated to, but not used by countries participating in the plan of distribution, will become available for projects by consumers in the United States and other countries. Japanese production has reached a level which will permit the export in 1953 of a small amount of refined nickel.

The estimated nickel availabilities for the first quarter of 1953 of 37,270 metric tons are only 219 tons or about 0·6% higher than for the fourth quarter of 1952. The recommended allocation, therefore, still falls considerably short of requirements, and the Committee's report to all Governments again stresses the need for strict economy in the use of nickel. The largest allocations are to the United States, 25,000 tons ; the United Kingdom, 5,400 tons ; France, 1,800 tons ; and the Federal Republic of Germany, 1,500 tons.

Personal News

MR. A. G. E. BRIGGS, Joint Assistant Managing Director of Tube Investments, Ltd. (Electrical Division), who was loaned to the Ministry of Supply as Deputy Controller of Supplies (Munition Production) in March, 1951, relinquished this appointment on December 31st, 1952, and has resumed his full-time duties with the Company. Mr. Briggs, as announced in the Queen's New Year Honours List, is to have the honour of Knight Bachelor conferred on him.

SOUTHERN FORGE, LTD., of Langley, Bucks., one of the Almin group of companies, announce that MR. L. E. YOUNG, Sales Manager, has been appointed a Director.

CAPT. R. T. PAUL has joined the Equipment Division of Mullard, Ltd., as Commercial Manager.

MR. R. W. COOPER, Chairman of the British Aluminium Co., Ltd., has resigned his Directorship as at December 31st, 1952 : he is succeeded as Chairman by VISCOUNT PORTAL OF HUNGERFORD. MR. E. F. O. GASCOIGNE has been appointed a Director of the Company.

THE United Steel Companies, Ltd., announce the following changes at three of their branches :— MR. C. R. BLICK has been appointed Assistant Commercial Manager of the Workington Iron and Steel Branch. At the Steel, Peech and Tozer Branch, Rotherham, MR. V. WATKINS, at present Maintenance Manager, is to be appointed Deputy Chief Engineer, and MR. C. WILKINSON, at present Assistant Cold Rolling Mill Manager, is to be appointed Cold Rolling Mill Manager in succession to Mr. J. Lees, who has left the Company. ENGINEER REAR-ADMIRAL C. W. LAMBERT, who is now General Works Manager at the Appleby-Frodingham Branch, Scunthorpe, is to retire at his own request on June 30th, 1953. It is intended that he shall be succeeded by MR. A. JACKSON, who is at present Works Manager (Steel) and Deputy General Works Manager. MR. T. P. LLOYD has been appointed Assistant Works Manager (Steel) with a view to his succeeding Mr. Jackson on July 1st.

MR. A. TRÉBUCQ has relinquished the position of Joint Managing Director of H. J. Enthoven & Sons, Ltd., the lead smelters and refiners, and has been appointed Deputy Chairman from January 1st, 1953. MR. K. L. COBB becomes sole Managing Director.

DR. G. E. GARDAM has resigned his position as Director of Research at the Design and Research Centre for the Gold, Silver and Jewellery Industries, to take up an appointment with Aluminium Laboratories, Ltd., Banbury, where he will be in charge of the Chemistry Section.

THE Directors of The Expert Tool & Case Hardening Co., Ltd., announce the appointment of MR. IVOR LLOYD as Vice-Chairman of the Company. Mr. Lloyd will retain his appointment as Joint Managing Director. MR. R. GRUT, Secretary of the Company for a number of years, has been appointed to the Board.

MR. A. BLYTH, General Manager of William Mills, Ltd., has been appointed a Director of the Company.

BRITISH INSULATED CALLENDER'S CABLES, LTD., announce the appointment of new Branch Managers at Bristol and Cardiff in succession to MR. R. S. GOUGH and MR. T. R. THOMAS, who have both retired. MR. T. L. PURVES takes over at Bristol and MR. L. R. GREET at Cardiff.

RECENT DEVELOPMENTS
MATERIALS : PROCESSES : EQUIPMENT

Water Bath Temperature Controller

To meet the need for means of controlling the temperature of oil or water baths, the Equipment Division of Mullard, Ltd., have recently made commercially available a Temperature Controller, Type E.7594. This instrument enables the temperature of water baths and similar apparatus to be controlled within fine limits, the response time being very rapid. It has the additional advantage of being simple in operation, and compact and

robust in construction. These features should make the instrument of particular value for use in connection with chemical analysis, and polarographic, conductivity, viscosity and refractive index measurements.

The sensitive element consists of a temperature-sensitive resistor, designed for direct immersion into the fluid to be controlled. This resistor forms one arm of an A.C. bridge network whose output is amplified and used to control a phase-sensitive circuit operating a relay. Since the phase of the bridge output changes very rapidly at the point of balance, quick action of the relay is ensured.

It is possible to use the instrument with any apparatus in which a water or oil bath is incorporated, but in order to make full use of the accuracy available, adequate stirring must be provided. The relay is of the single-pole, double-throw type, and can switch up to 1 amp. at 230 volts, so that most heating elements used on water baths can be effectively operated. The Type E.7594 operates from 50 c/s., 110–120 or 200–250 volt supplies, with a power consumption of 25 watts.

The instrument has a temperature range of 15–75° C., covered in three steps. A large dial allows the setting point to be precisely located and locked in position. Although the calibrated accuracy of the scale is ±1° C., it is possible to control the temperature to within ±0·02° C. about the working point.

A four-position range switch is provided, which alters the value of the resistor in the fixed or standard arm of the bridge circuit. The adjacent arm of the bridge contains the temperature-sensitive element, whilst the remaining two arms are provided by the potentiometer balance control. The fourth position of the range switch connects the bridge to a socket on the front panel of the instrument. This enables a precision external resistor to be connected into the bridge in place of the internally-connected standard resistor. By keeping the external resistor at a constant temperature, a greater accuracy of control can be effected. Moreover, through the choice of external resistance values, the range of the instrument can be extended to cover any temperature between −50° C. and +80° C. At the lower position, however, the range covered by the fine control is only 10° C.

Mullard, Ltd., Century House, Shaftesbury Avenue, London, W.C.2.

Magnetic Crack Detecting Equipment

THE range of crack detecting equipment made by The Magnetic Equipment Co., Ltd., has been recently extended by the provision of a universal machine for dealing with the most complicated shapes and with shafts up to 5 ft. in length to special order.

The machine shown in the illustration is available in two types, MCC for current-flow testing and MCD for current-flow and magnetising tests, and comprises two sliding heads capable of opening from 2 in. to 5 ft. or more. For repetition work, one head can be clamped in position and the other one moved and held by an air-operated pressure cylinder, leaving the operator two hands free to handle the work.

The inspection of large castings and forgings frequently necessitates the work being laid on a tray and solenoids

formed by wrapping a few turns of heavy flexible cable around different parts in turn. To enable this to be done, the machine is provided with rear terminals and a heavy current changeover switch so that false readings cannot be obtained should the heads or cables be accidentally short-circuited by other work. Provision is also made for plugging-in magnetic leeches for speedy operation in current-flow testing of work adjacent to the machine.

The Magnetic Equipment Co. Ltd., Lake Works, Wicor, Portchester, Hants.

CURRENT LITERATURE

Book Notice

PIONEERS OF A CENTURY—1852–1952

UNDER the above title, Samuel Osborn and Co. Ltd., have published a history of the growth and achievement of the firm over the past 100 years. The founder, Samuel Osborn, was born in 1826 and on leaving school at the age of 15 he found employment with a well-known Sheffield drapery concern. Soft goods did not appeal to him, however, and at the age of 19 he moved to Thomas Ellin and Son, manufacturers of a variety of tools. This was not the branch which attracted him most as he was keen on handling files, saws, shear blades, etc., and on the manufacture of steel for them. To this end, he joined Henry Rossell and Co., where he formed many connections which were never broken. In April, 1852, he started in business for himself, files being his first product. Some idea of the small scale on which Osborn started can be gathered from details given of entries in the first cash book he kept.

From this small beginning, the company gradually increased its activities until it grew into one of the leading Sheffield firms, producing all forms of tool steels, special alloy steels, a wide variety of engineers' tools, steel castings and forgings. During the war, the number of employees rose to 3,000, the general average in the post-war years being 2,500, which gives some idea of the growth of the firm.

One of the outstanding events in the history of the company was Samuel Osborn's decision to take over all Mushets' processes and steels and to market them. The transfer began late in 1870, and by the following year all arrangements had been made, including the transfer to Sheffield of some of the workmen from the works at Coleford. Although "R. Mushet's Special Steel" as the self-hardening steel was called, had already achieved a measure of success, in association with Osborns progress was gradually made until it swept the engineering world and revolutionised machining practice. For many years this steel was regarded as the best self-hardening steel available.

The story presented is a fascinating one and the many excellent portraits of the various leaders of the business, and of the works and processes, adds greatly to the interest. The author, Mr. T. A. Seed, and printers, are to be congratulated on a very worthy publication.

Trade Publications

ALTHOUGH the past decade has seen aluminium advance to become one of the foremost engineering materials, its progress has been so rapid and so extensive as to outstrip its literature. Standard engineering reference books are still largely pre-occupied with traditional materials, and do not meet the needs of engineering students and others who want to know the facts without having to wade through specialised books. For this reason, Northern Aluminium Co., Ltd., have published, under the title of "About Aluminium," a collected edition of a series of articles written to provide a brief introductory survey of the characteristics of the metal and its alloys. Apart from some notes on the past, present and probable future of aluminium and its alloys the articles comprise mainly a short account of specific physical and mechanical properties.

PUBLICATION 25, "Heavy Fan Engineering," has been prepared by Keith Blackman, Ltd., Tottenham, London N.17, to emphasize the scope of Tornado products in the heavier classes of engineering. Such products involve heavy plate construction, large shafts and bearings, and high speeds and pressures, whilst special designs and materials are required to satisfy stresses set up by high peripheral speeds or high temperature applications. The types of fan illustrated include multivane centrifugal fans, mill exhausting fans, induced draught fans, alternator cooling fans, gas boosting fans, multi-stage turbo blowers, axial fans and mine ventilating fans.

WE have received from Sanderson Brothers & Newbould, Ltd., Newhall Road, Sheffield, a copy of a new leaflet, M.E.38, describing the M.C.V. Steel manufactured by the Company. It is a medium-carbon, low-alloy steel combining toughness and hardness with high tensile strength, and is recommended for components subjected to heavy loads, severe torsional strains, or sudden shocks. Details are given of the appropriate conditions for working and heat treatment, and typical test results are included.

Books Received

"Structure of Metals—Crystallographic Methods, Principles and Data," second edition. By Charles S. Barrett, Ph.D. Metallurgy and Metallurgical Engineering Series. 661 pp. inc. numerous illustrations and index. 1952. McGraw-Hill Book Company, Inc. 72s. 6d.

"Welding Practice," Vol. II. "Welding of Ferrous Metals." Edited by E. Fuchs, M.A., A.M.I.Mech.E., and H. Bradley, M.Met. 198 pp. inc. 22 tables, glossary, numerous illustrations and index. London, 1952. Butterworths Scientific Publications in association with Imperial Chemical Industries, Ltd. 22s. 6d. By post 1s. extra.

"Mechanical World Year Book." 1953. 360 pp. inc. numerous tables. Manchester, 1952. Emmott & Co. Ltd. 3s. 6d. net.

"Nichtmetallische Anorganische Überzüge," by Willi Machu. 404 pp. inc. indices and 153 illustrations. Vienna, 1952. Springer-Verlag. 97s.

"Lighting in Industry." Electricity and Productivity Series, No. 2. 154 pp. inc. index and 85 illustrations. London, 1952. British Electrical Development Association. 8s. 6d. net, or 9s. inc. postage.

"Aide-Mémoire Dunod Métallurgie." By R. Cazaud. 65th Edition, 1953. 324 pp. inc. 42 illustrations. 48 pp. of formulae and tables. Paris, 1952. Dunod. 450 F.

"Fatigue and Fracture of Metals." A Symposium held at The Massachusetts Institute of Technology, June 19–22, 1950. Edited by William M. Murray, with a foreword by Jerome C. Hunsaker. 313 pp. Massachusetts, New York and London, 1952. The Technology Press of The Massachusetts Institute of Technology and John Wiley & Sons, Inc. Chapman & Hall, Ltd. 48s. net.

METALLURGICAL DIGEST

Powder Metallurgy Parts in High Temperature Applications

By Julius J. Harwood

THE urgent need for conservation of critical alloying elements has led to the development of leaner alloy compositions for gas turbines now in production. The need for materials of superior high temperature strength properties is being approached through development of new refractory alloy systems, development of metal-bonded refractory compounds commonly called cermets, and development of materials useful for artificial cooling techniques, e.g., permeable materials for sweat cooling. In all these various developments, powder metallurgy methods and techniques are playing significant and important roles.

Copper Alloy Infiltrated Iron.—The development by the American Electro Metal Corporation of the copper-alloy infiltrated iron compressor stator blade represents the first major competitive introduction of powder metallurgy in the gas turbine field. This stator blade is made by moulding iron powder by means of a multiple action die into a preform shape. The preform is sintered and then coined to the exact dimensions of a compressor blade with the thin trailing edge and the thicker leading edge. After coining, the porous blade is infiltrated with a copper alloy to 100% density and heat treated to develop the required strength properties. Tensile strengths of 90,000 lb./sq. in. with elongations of 8% have been reported. This compressor stator blade is giving satisfactory service in at least one industrial gas turbine. It has also been tested as a rotor material, for which the strength requirements are higher, and indications are that it may prove satisfactory for such applications. Research is in progress with a view to improving the high temperature strength and impact properties of the material by appropriate alloying additions.

Titanium Alloys.—Titanium alloys are being used in limited production as compressor disc materials; these discs operate at a temperature greater than 350° F. Titanium alloys are also being evaluated for use as compressor blade materials, and the indications are that they may be satisfactory for the first few compressor stages. It must be noted that any high temperature operations with titanium, such as sintering, must be done under vacuum or inert atmospheres.

Sintered Aluminium Powder.—An interesting Swiss development is a new sintered aluminium product which shows potentialities for use at temperatures of 800° F. This material is produced by cold pressing aluminium powder of fine particle size into briquettes under a pressure of 20–50 kg./sq. mm., sintering the briquettes at temperatures of 900–1,100° F., followed by further hot pressing under 50 kg./sq. mm., and finally extruding the material into rods. These rods can be further cold or hot worked into sheets, shapes or drop forgings. The powder is produced by the Hametag process in an atmosphere low in oxygen. About 50% of the flake particles produced have one dimension below 2 angstroms, and from the standpoint of metallic impurity the material contains between 10 and 20% by weight of oxide. Presumably each particle is surrounded by a layer of aluminium oxide. Exposure to temperatures as high as 900° F. for as long as 100 hours results in little or no change in the room temperature tensile properties. Several industrial concerns are experimenting with this material for component applications in standard engines and, in view of its high temperature strength properties, consideration is also being given to its use as a compressor blade material.

The major part of high temperature material research and development is being directed to the turbine stage of jet engines, since this is where potential gains in performance can be achieved. At present, blades are being welded or mechanically fitted into discs to form turbine wheels. Blade materials must have high oxidation and erosion resistance, high creep and rupture strength over a range of temperature, high fatigue strength at operating temperatures, and resistance to thermal shock. Three different approaches to the turbine blade materials problem offer considerable promise, these are the development of cermets; the development of transpiration-cooled blades; and the development of molybdenum-base alloys. In all these powder metallurgy is playing an important role.

Cermets.—In the field of cermets, metal-bonded carbides, borides, nitrides, aluminides, silicides, and oxides are being investigated. Procedures commonly used are conventional pressing and sintering operations, hot pressing, hydrostatic pressing methods using oil and rubber bags, rubber moulding techniques to obtain uniform densities, or extrusion methods using a fugitive plasticiser.

Some of the most promising cermets are the cemented titanium carbide compositions. These metal-bonded titanium carbides exhibit strength properties up to 1,800° F. and oxidation resistance and thermal shock characteristics which make them potentially useful turbine blade materials for present day engines and which hold out a real hope for boosting turbine operating temperatures several hundred degrees. Titanium carbide blades fabricated according to present designs, have run satisfactorily in engine tests for over 100 hours. This is significant, considering that present blade designs are far from suitable for the use of these materials. The ultimate use of these non-ductile materials will depend upon design innovations that will avoid their deficiencies and make maximum use of their strength properties.

Materials for Sweat Cooling.—The use of artificial cooling systems, so that the blade is maintained at a temperature appreciably lower than that of the gas, is being investigated. One efficient method of accomplishing this objective is the use of transpiration, or sweat cooling. Transpiration cooling consists of forcing a stream of coolant, either gas or liquid, through a porous body, in the direction opposite to the heat flow. The cooling medium gradually increases in temperature while passing through the porous body and finally reaches the inner wall surface, where it forms a protective

From *Materials and Methods*, August, 1952, adapted from a paper delivered at the Eighth Annual Meeting of the Metal Powder Association, April, 1952.

layer. Sweat cooling has been shown to yield larger temperature drops than any other method of cooling which has been investigated.

The major problem involved is to develop porous alloys having maximum permeability and minimum porosity in order to obtain the high strengths required. Three general techniques are now being investigated for the preparation of controlled permeability bodies—loose powder sintering, cold pressing and sintering, and extrusion of metal powders using plasticisers or carriers.

Molybdenum-base Alloys.—Another promising approach has been the development of molybdenum-base alloys for high temperature application. Powder metallurgy techniques have advanced to the stage where sintered and pressed molybdenum shapes measuring up to 6 in. sq., 4 ft. long and weighing over 400 lb. are not uncommon. Hydrostatic pressing techniques have made feasible the production of powder metallurgy ingots weighing up to 700 lb.

At temperatures above 1,600° F. the creep and stress-rupture properties of commercially pure molybdenum are superior to any high temperature alloys. These high temperature properties vary considerably with the source of molybdenum powder, purity of powder, method of consolidation, fabrication history and other factors. In order to obtain superior high temperature strength properties, parallel research programmes are in progress for the development of molybdenum-base alloys by both arc melting and powder metallurgy techniques. Alloys have already been developed which show outstanding stress-rupture properties. The recrystallisation temperatures of some of these alloys are about 1,000° F. higher than for commercially pure molybdenum.

Several obstacles still require to be overcome before molybdenum alloys can receive widespread acceptance. Satisfactory protective coatings are needed to prevent the rapid oxidation which molybdenum and its alloys undergo. Certain brittle characteristics which cause welding, fabrication and service difficulties must also be overcome. Molybdenum turbine blades are being developed and reports indicate that such blades coated with protective coatings have been run in engine tests for over 100 hours.

New High Temperature Alloy

A NEW alloy for high temperature service, which contains no cobalt and has good forming characteristics, has been announced by the Haynes Stellite Co. It has been named Hastelloy Alloy X. Its nominal composition is stated to be 22% chromium, 45% nickel, 9% molybdenum, 0·15% max. carbon, and the remainder iron. Tests have shown this new alloy to have excellent forming characteristics, good high temperature properties, and high resistance to oxidation. It is being manufactured in the form of sheet, plate, bars, wire and precision investment castings.

Although testing of Hastelloy X is still in the initial stages, some results are available for comparison with the properties of Multimet, a material on which considerable work has been done. Testing programmes are in progress to establish creep properties from 1,200° to 1,800° F., rupture life at 1,650 and 1,800° F., thermal shock characteristics and embrittlement effects. Investigation of the relative oxidation resistance of the new alloy in comparison with other high temperature materials is in progress. Preliminary tests have indicated that it has high resistance to oxidation. A comparison of wrought Hastelloy X and Multimet (N155) alloys, as a result of short time tensile tests and creep rupture tests at various temperatures, is given in the accompanying table; the tensile properties of precision investment cast Hastelloy X are also given.

From *Materials and Methods*, August, 1952, 98–99.

COMPARISON OF WROUGHT HASTELLOY X AND MULTIMET (N155) ALLOYS

Alloy	Nominal Composition, %	Temp. ° F.	Short Time Tensile Properties			Creep Rupture Properties		
			Tensile Strength 1000 Psi	Yld. Str. 0·2% Offset, 1000 Psi	Elong. % in 2 In.	Stress	Rupture Life, Hr.	Elong. %
Hastelloy X	0·15 C max	Room	116	57	44·5	—	—	—
	22 Cr	1200	—	—	38	15	500*	0·285
	9 Mo					45	90	20·0
	45 Ni	1350	68	—	31	—	—	—
	Rem Fe	1500	48	—	37	18	—	35·0
		1650	31	—	41	—	30	—
		1800	20	—	41	—	—	—
Multimet ..	0·08–0·16 C	Room	116	57	42	—	—	—
	20–22·5 Cr	1200	—	—	35	15	500*	0·175
	2·5–3·5 Mo					45	175	11·0
	18·5–21 Co	1350	55	—	39	—	—	—
	2–3 W	1500	37	—	39	18	80	28·0
	19–21 Ni	1650	27	—	40	—	—	—
	0·10–0·20 N	1800	17	—	37	—	—	—
	0·75–1·25 Co+Ta							
	Rem Fe							

* Tests discontinued.

SHORT TIME TENSILE PROPERTIES OF PRECISION INVESTMENT CAST HASTELLOY X

Test Temp. F.	Ult. Str., Psi.	Yld. Str. at 0·2% Offset, Psi.	Elong. % in 2 in.
Room	71,000	44,000	22·0
1200	52,000	—	16·0
1350	49,000	—	17·0
1500	47,000	—	19·0
1650	36,000	—	25·0
1800	20,000	—	35·0

The 'Udytal' Process of Direct Nickel Plating on Aluminium

By J. Bary

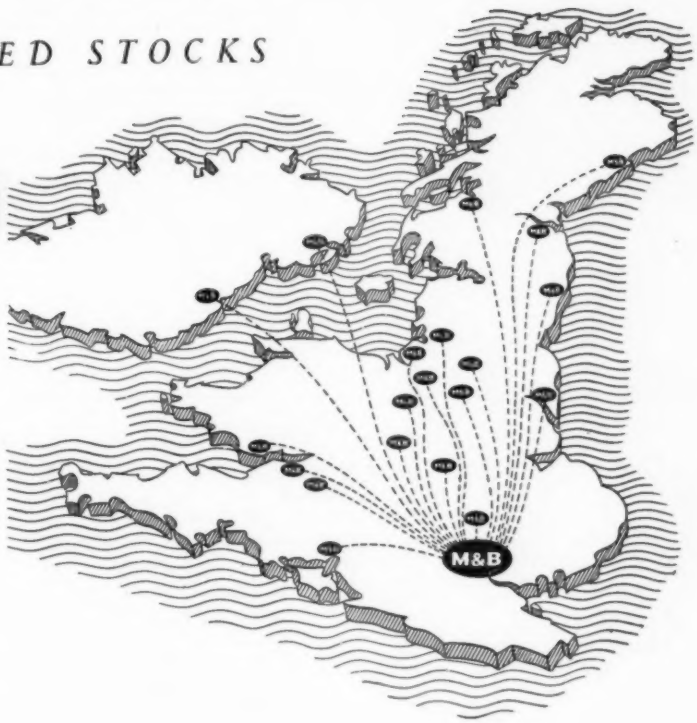
THE "Udytal" process, developed by the Societe Continentale Parker, makes use of the zincate pretreatment of the aluminium surface, but avoids the subsequent intermediate copper plating. Instead, the zincate treated surface is plated directly in a special nickel bath, the composition of which is such that contamination by relatively large amounts of zinc can be tolerated. Plating is continued for 15 mins. at 1·5 amp./sq. dm., a 5μ thick coating being deposited. After rinsing, this is followed by the deposition of a 15μ thick bright nickel coat from a "Udylite" bath and finally by chromium plating. Compared with the normal zincate process with intermediate copper and nickel plating prior to chromium plating, the "Udytal" process cuts the total number of operations from 28 to 18 and eliminates the need for intermediate polishing.

From *Revue de l' Aluminium*, **29**, 16–17, January, 1952. Abstracted in *Light Metals Bulletin*, **14**, No. 19, 749, September, 1952.

FOR PROMPT DESPATCH

FROM PRE-PACKED STOCKS

. . . specify M&B



The containers of **M&B** Laboratory Chemicals and Reagents are standardized to those sizes in most regular demand, and pre-packed stocks of every item are held at Dagenham and by stockists throughout the country. In this way, we are able to ensure that orders are promptly dealt with.

The range comprises over 500 different specifications, each of which is carefully checked in manufacture and clearly printed on the appropriate label. Specially designed containers provide maximum protection in transit and storage, and plastic screw-caps are fitted for convenience in handling.

M&B brand

LABORATORY CHEMICALS AND REAGENTS

MANUFACTURED BY: **MAY & BAKER LTD · DAGENHAM · ENGLAND** · *TELEPHONE: ILFORD 3060 · EXTENSION 40*

ASSOCIATED HOUSES: BOMBAY · LAGOS · MONTREAL · PORT ELIZABETH · SYDNEY · WELLINGTON · BRANCHES AND AGENTS THROUGHOUT THE WORLD

For X-ray Darkrooms

Two items from the 'Kodak' range that make the production of industrial radiographs quicker, easier, more certain. There's 'Kodak' equipment to speed the operator's task at every stage of darkroom production.

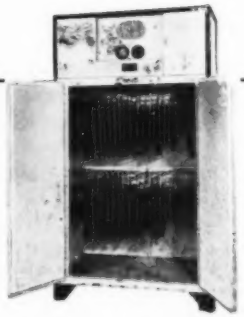
High-output Precision Processing

Developing, spray-rinsing, fixing and washing all in one self-contained unit. Thermostatically-controlled water-jacket surrounds processing tanks. Output: 50-60 full-size (14 × 17 in.) radiographs an hour. Developing tank capacity 5 gallons (Model 46) or 10 gallons (Model 146).

'Kodak' X-Ray Processing Unit

Rapid Dust-free Drying

Safe inside a 'Kodak' drying cabinet radiographs dry quickly and cleanly. The Model X accommodates 52 full-size (14 × 17 in.) radiographs in hangers. Four-way electric switch controlling fan and heaters, and adjustable entrance grid allow wide control of temperature. Normal drying time approximately 45 minutes.



'Kodak' Drying Cabinet Model X

KODAK LIMITED • *Industrial Sales Division* • **KODAK HOUSE** • **KINGSWAY** • **LONDON W C 2** 'Kodak' is a registered trade-mark

Ether-Wheelco *ELECTRONIC CONTROLS*

The use of Electronics as the basic principle of our automatic controller enables more rapid and accurate control to be obtained than is possible with any other system.

Fig. 1 illustrates the "CAPACITROL" giving On-Off or High-Low control. Other types giving two-position and proportional control are known as the "MULTRONIC" and "PROPORTIONAL CAPACITROL."

All these instruments use electronics to automatically control temperatures with the speed of light, great accuracy and no interference with the measuring system. They are faster, simpler and more accurate than the Chopper Bar type formerly used.

Fig. 2 shows the way by which the science of electronics is used to automatically control temperatures.

A light aluminium flag "C" passes between two coils "A" of the electronic system. When the flag enters the sphere of influence of the coils a movement of a few thousandths of an inch is sufficient to switch the control system off or on. By moving the coils attached to the pointer "B," the control position can be readily adjusted.

Fig. 1

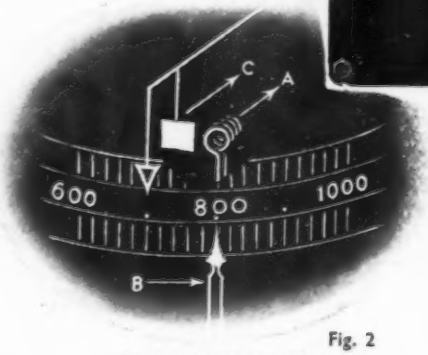


Fig. 2

Send for LIST No. 250.

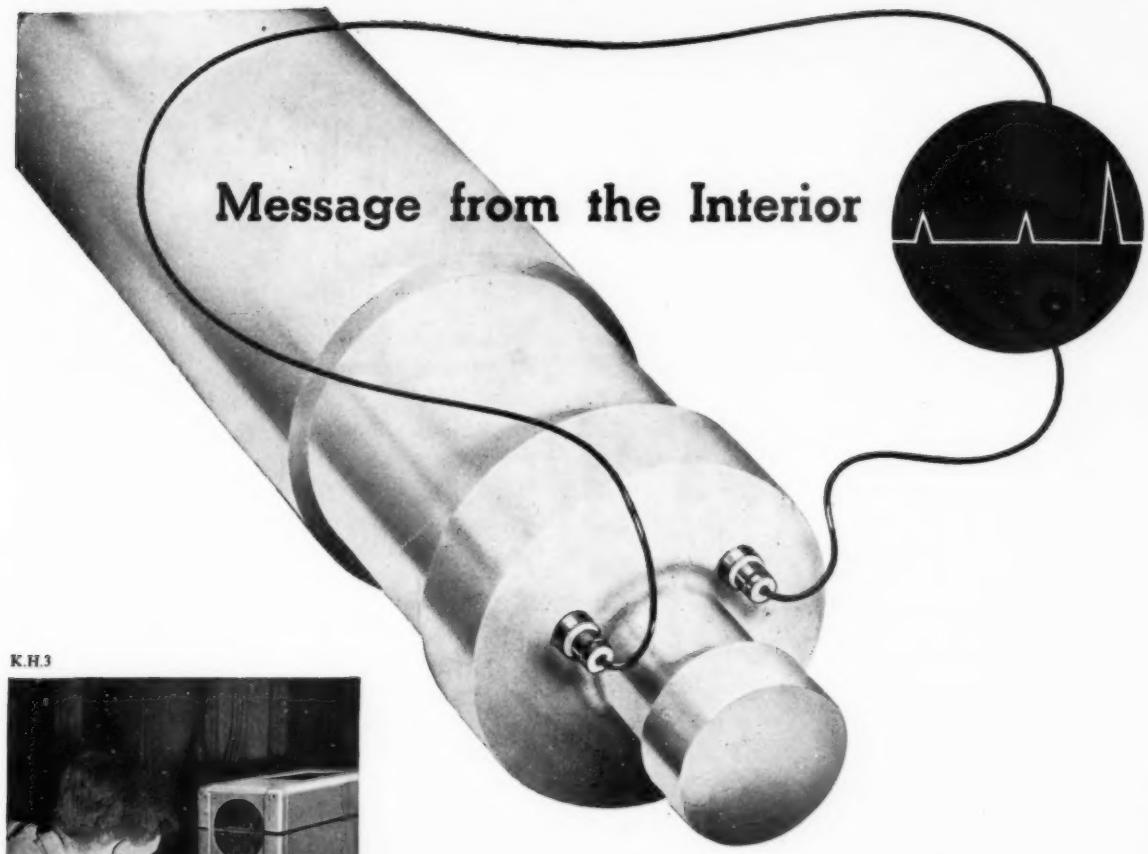
The "CAPACITROL" (E.W.22

Automatic Temperature Controller capable of controlling electric, gas and oil-fired furnaces and apparatus utilising the On-Off or By-Pass system of control.

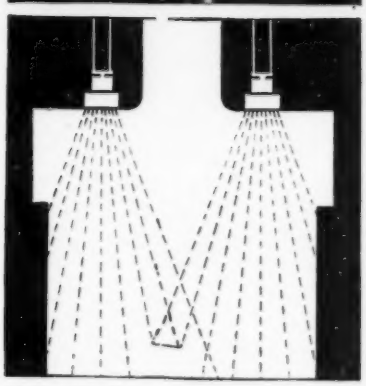
ETHER LTD
Tyburn Road, Erdington
BIRMINGHAM 24
Telephone ..... EASt 0276-7

Holdens

Message from the Interior



K.H.3



THE HUGHES Mk. 4 SUPERSONIC FLAW DETECTOR enables flaws in metal—whether in billet form or as a finished component—to be detected unerringly without damaging the metal itself. Many cracks difficult to detect by radiographic methods are easily found. Moreover the equipment is portable, easy to operate and indicates the actual position of the flaws and not merely their presence.

A narrow beam of supersonic energy is directed into the metal under inspection by a small probe (the transmitter). Energy reflected by any flaws in the path of the beam and from the opposite boundary of the material is picked up by a second probe (the receiver) and its presence shows on a cathode ray tube, which thus indicates the relative positions of flaw and material boundary.

KELVIN HUGHES
PRECISION INSTRUMENTS

KELVIN & HUGHES (INDUSTRIAL) LTD., 9, CAXTON STREET, LONDON, S.W.1

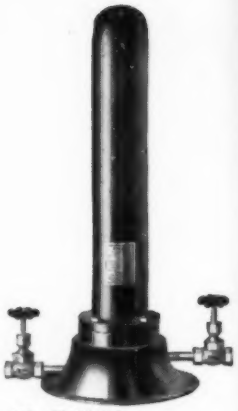
BAKER PLATINUM LIMITED

deoxo

CATALYTIC GAS PURIFIER

1,000 c.f.h. Model

The Baker ' Deoxo ' Gas Purifier provides a highly efficient and trouble-free catalytic method of removing unwanted oxygen from hydrogen. Also the removal of either of these gases from Nitrogen, Argon, Helium, Neon, Carbon Dioxide and saturated hydro-carbons. The ' Deoxo ' standard Purifier will remove up to 1% oxygen or 2% hydrogen. High purity is consistently produced, the remaining impurity being less than one part per million (.0001%).



200 c.f.h. Model

5 c.f.h. Model

OPERATIONAL ADVANTAGES

As catalytic reaction commences at room temperature, this purification system offers the following advantages :—NO auxiliary heating required ● NO water cooling required ● NO operating expenses ● NO maintenance expenses.

★ *A copy of the illustrated publication, giving full details of the ' DEOXO ' process, will be forwarded on application. Technical representatives are always available for consultation and advice.*

BAKER PLATINUM LTD.:, 52 HIGH HOLBORN, LONDON, W.C.1. *CHAncery* 8711

Looking for trouble

high above London

ILFORD Industrial X-ray films are always looking for trouble—at all levels. This mobile X-ray unit is investigating the soundness of a welded structure high above London—a type of inspection that calls for a completely reliable sensitised material. The fact that so many of the radiographs taken during the erection of important engineering projects are made on ILFORD Industrial X-ray films is a convincing tribute to their consistently high quality.

ILFORD INDUSTRIAL X-RAY FILM TYPE A
A general-purpose film whose very high speed, exceptional latitude and good contrast when used with calcium tungstate screens make it particularly suitable for the examination of ferrous welds and heavy castings whether with X-rays or gamma rays.

ILFORD INDUSTRIAL X-RAY FILM TYPE B
A fast film designed for direct exposure to X-rays or for use with lead screens. Recommended for the radiography of a wide range of castings and welds in light alloy or steel where the aim is the detection of fine detail with economical exposure times.

ILFORD INDUSTRIAL X-RAY FILM TYPE C
A special high-contrast, direct-exposure film of medium speed and extremely fine grain, intended for the radiography of magnesium and aluminium castings where very fine detail must be recorded, and for the examination of all materials having a low X-ray absorption coefficient.

ILFORD INDUSTRIAL X-RAY FILM TYPE G
A new ILFORD product and the fastest film yet made for use with or without lead screens. Three times as fast as the Type B film, yet with very little increase in graininess, it is ideal for the examination of heavy castings and assemblies in steel or bronze either with X-rays or gamma rays.

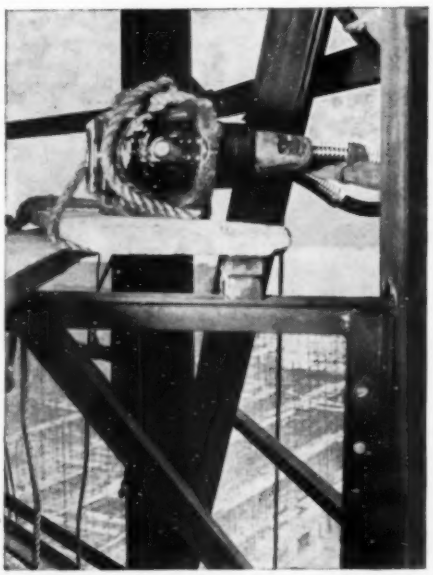


Illustration shows Newton Victor Raymax 140 kV. Industrial X-ray Unit lashed in position for radiography of welds during construction of the welded heat-storage tower for the Pimlico District Heating Scheme.
Reproduced by courtesy of Messrs. Newton Victor Limited.

ILFORD Industrial X-ray Films

ILFORD LIMITED · ILFORD · LONDON

HYDRAZINE HYDRATE

is now in full production in the new plant

of our associate company

GENATOSAN LTD.

AVAILABLE FOR IMMEDIATE DELIVERY IN
100%, 90%, and 60% strength

WHIFFENS

fine chemicals for industry

WHIFFEN AND SONS LTD., CARNWATH ROAD, LONDON, S.W.6
Telephone: RENown 3416 *Telegrams: Whiffen, Walgreen, London*

H.1

SOAP FILM GAS ANALYSIS

A NEW RAPID ACCURATE SIMPLIFIED EQUIPMENT

This New Soap Film Apparatus achieves percentage analyses of almost any gaseous mixtures with unique simplicity. The alternation of special soap film gas meters with reagent scrubbers—all simultaneously controlled—enables constituent gases to be determined merely by sliding a lever and taking readings.

Especially Designed for Town Gas, this apparatus constitutes a major advance in procedure. Gaseous mixtures may be passed through the system, under their own pressure or by means of the fitted pump, with no appreciable back pressure—and without temperature corrections having to be made.

Furnaces Provided at the side of the apparatus, for use in oxidising some constituents, are thoroughly insulated from the system. All fittings and controls are designed to provide the maximum degree of efficiency.

Please Write for further details and for a reprint of the paper by W. J. Gooderham which fully describes this apparatus.

DELIVERY EX STOCK.

GRIFFIN & TATLOCK LTD.

SCIENTIFIC INSTRUMENT MAKERS SINCE 1826

LONDON: Kemble Street, W.C.2.
MANCHESTER: 19, Cheetham Hill Road, 4.
GLASGOW: 45, Renfrew Street, C.2.
EDINBURGH: 8, Johnston Terrace, 1.
BIRMINGHAM: Standley Belcher & Mason Ltd., Church St., 3.

Modern Microscope Techniques

–by incident phase contrast and incident polarised light are catered for by the

BECK *Vertiphase* ILLUMINATOR

ADAPTABLE TO STANDARD METALLURGICAL MICROSCOPES

Descriptive Booklet from

R & J BECK LTD · 69 MORTIMER ST · LONDON · W.1

IPco

Specify

"INDUSTRIAL"

CONTROLLING PYROMETERS

on your next furnace installation

This advanced controller has achieved outstanding success by its simplified mechanism, which ensures high accuracy, close temperature control and consistently high performance.

THE INDUSTRIAL PYROMETER CO. LTD.
GOOCH STREET, BIRMINGHAM, 5.
Telephone: MIDland 5470

LABORATORY METHODS
MECHANICAL · CHEMICAL · PHYSICAL · METALLOGRAPHIC
INSTRUMENTS AND MATERIALS
JANUARY, 1953 Vol. XLVII, No. 279

Recent Developments in Metallurgical Analysis
II.—Titrimetric Analysis

By T. S. West, B.Sc., Ph.D., A.R.I.C.
Chemistry Department, The University of Birmingham.

Many advances have been made in analytical methods during the past few years. The present series of articles reviews some of these developments under the general headings: I—Electrochemical Analysis; II—Titrimetric Analysis; and III—Gravimetric Analysis. Such is the volume of papers forthcoming in those three main divisions, however, that it is only possible to touch on the more interesting developments which have appeared within the past few years, although references have been made to work previous to this period where it has been felt necessary to trace the logical development of some of the methods.

MANY new reagents, and many important modifications to existing titrimetric methods have been proposed during the past few years, but mention can be made of only a few of them in the space available.

NEW TITRANTS

Quinquevalent Molybdenum

It is a fault in many strong oxidants and reductants that they are highly unstable and require frequent standardisation. As examples of this, we have permanganate, on the one hand, and titanous sulphate, on the other. A powerful new oxidant was proposed in 1948 which is claimed to be relatively stable in normal storage under atmospheric conditions.

The reagent—quinquevalent molybdenum[1]—was prepared by electrolytic reduction of molybdic acid in a medium of 8 N hydrochloric acid. Its stability was such that a reagent solution in 8 N acid underwent a decrease in equivalence of 0·9% in seven days, and neither heat nor light was found to affect this stability. Because of the high redox potential at such high acidity, however, such a solution was used only as a stock for the preparation of a reagent solution in 2 N acid. This solution was considerably less stable.

Reductimetric titrations of ferric iron in hydrochloric or sulphuric acid were effected potentiometrically, using a platinum indicator electrode against a calomel reference electrode. In titrations of iron in hydrochloric acid, an elevated temperature of 80° C. was necessary, and the maximum permissible concentration of chloride ion was 0·1 N. Good results were claimed for iron in sulphuric acid concentrations varying from 0·1 N to 4 N.

Titration of vanadate with the quinquevalent molybdenum reagent was also possible. A maximum increase in e.m.f. of 100 mV/0·1 ml. was recorded, equilibrium being attained over an interval of a few seconds.

The determination of hexavalent cerium, ferric iron, dichromate and vanadate was studied, and it was found possible to determine mixtures of two or three together using the new reagent. Favourable results were reported for mixtures of cerium^{VI} and iron^{III}; cerium^{VI} and vanadium^{V}; and chromium^{VI} and iron^{III} at the 0·1 N level, using a 0·1 N reagent at room temperature in a hydrochloric acid medium. An inert atmosphere of carbon dioxide was necessary when iron^{III} was present. In this respect, however, the reagent is in no way inferior to the classical direct titrants for ferric iron, viz., titanous and stannous chlorides, which have to be stored, as well as used, in an inert atmosphere.

The method of standardisation of the quinquevalent molybdenum reagent was to titrate in hot solution with standard ceric sulphate solution. The authors also recorded a potentiometric titration of iodate and bromate solutions at room temperatures, as well as an alternative standardisation method against potassium dichromate.

Mercurous Nitrate

Another new reagent for the determination of ferric iron has been examined by Belcher and West[2]. This reagent effects all the analyses carried out by the previous reagent and, apart from having a much wider range of application, is very easily prepared, is indefinitely stable, and can be used with a visual indicator, or with a potentiometric indication of the end-point in solutions which are highly coloured.

Most titrimetric methods for ferric iron involve a previous reduction to the ferrous state by means of a Jones reductor, or some such device, followed by the use of an oxidimetric reagent such as potassium dichromate or permanganate. Apart from the reagent under discussion, only three direct titrants are available, i.e., titanous, stannous and chromous chlorides and, as indicated previously, these reagents must be stored and used in inert atmospheres. Mercurous nitrate has the advantage that it effects quantitative reduction of ferric iron at ordinary temperatures in the presence of an excess of ammonium thiocyanate, without the necessity for an inert atmosphere or a potentiometric end-point. The reaction was found to be stoichiometric over the

range of iron concentrations examined, and amounts of iron varying from 300 μg. to 0·3 g. were determined.

The originators of the reagent, Bradbury and Edwards[3] made only a limited examination of it, but Belcher and West outlined the limitations of the method and extended its use to the determination of many ions other than ferric iron. Titrations of iron were effected in sulphuric, nitric and hydrochloric acids: the optimum concentration of nitric acid was 2·5 N, while the figures for sulphuric and hydrochloric acids were 3·8 N and 0·8 N. Larger amounts of acid could be tolerated, however. Thus, titration could be carried out in 2 N hydrochloric acid by using twice the normal amount of thiocyanate. The only common metals which were found to interfere with the determination were copper and molybdenum. Large amounts of cobalt and bismuth interfered by obscuring the visual end-point, but titration could still be carried out potentiometrically. The interference of ions such as fluoride, oxalate and pyrophosphate, which form complexes with ferric iron, was readily overcome by using higher concentrations of ammonium thiocyanate in the titration medium, but the compounds formed with ferro- and ferri-cyanides were more stable than the ferric thiocyanate complex, so that these ions interfered with the determination.

By use of a solution of ferrous sulphate, it was found possible to determine oxidants such as dichromate, ceric sulphate, vanadate, permanganate, chlorate, peroxide and persulphate by titration of the ferric iron formed in the reaction of these ions with the ferrous solution; the reaction with dichromate provided a primary standard for the reagent. An indirect method for the determination of lead and barium, based on precipitation of these metals as their insoluble chromates, was suggested by the authors, but not examined.

In the course of investigating the interference of various cations in the titration of ferric iron with mercurous nitrate, it was noted that when copper was present, high titres were obtained. The increase in titre was due to the fact that in the presence of the large excess of ammonium thiocyanate, cupric copper oxidised ferrous iron. Use was made of this to evolve a new titrimetric method for copper. In this method an excess of ferrous sulphate was added to the cupric solution followed by a large excess of 40% ammonium thiocyanate. The iron was oxidised instantaneously to the ferric state, and was determined by direct titration with mercurous nitrate. Although this reaction is the reverse of that usually observed, where the cuprous ion reduces the ferric ion, it has been found that the large excess of thiocyanate was responsible for this anomaly, and the reaction was explained on theoretical grounds.

Tripotassium-ditungstic-enneachloride

An extremely powerful reductant has been proposed by Czechoslovakian workers[4]. The reagent, tripotassium-ditungstic-enneachloride, $K_3W_2Cl_9$, reduces mercuric salts to the mercurous state, and even to free mercury, while silver salts are reduced to metallic silver and ceric salts to cerous. The salt is prepared by reduction of a mixture of tungstic acid and potassium tungstate in hydrochloric acid with metallic tin, followed by precipitation of the bright green crystals of $K_3W_2Cl_9$ at 0° C. by saturation of the solution with gaseous hydrogen chloride. The reagent solution, which may be stabilised against atmospheric oxidation by addition of traces of alcohols, citric acid or a soluble dioxime, has several advantages over titanous chloride. Thus, for example, it is readily obtained in a pure state, and the crystals are stable and non-hygroscopic. It can be used for titrations of neutral solutions without showing any tendency to hydrolyse.

The redox potential of the reagent was similar to that of titanous chloride, and, as with the latter, an inert atmosphere was necessary in carrying out titrations. Although ferroin and cacotheline were used as indicators in certain cases[5], a potentiometric method was generally required for location of the end-point. The authors[4] used the reagent for the titration of copper, iron, copper and iron together, chromium, chromium and iron together, iron and cerium, obtaining good results in all cases. They suggested further applications of the reagent to the determination of various other ions including selenite, ferricyanide, molybdate and arsenate.

Trivalent Manganese

Manganic sulphate was proposed as an alternative oxidising agent to permanganate by Ubbelohde[6]. The reagent has an advantage over the latter titrant, in that it can be used for the titration of ferrous iron in the presence of the chloride ion. However, as it is even more unstable than permanganate, the reagent has received scant recognition. Attempts have been made by others[7] to obtain a more stable form of the trivalent manganese ion, by the use of various complexing agents. Pyrophosphate was found to stabilise the ion in 0·1 N solution for a considerable period of time, and the reagent was used to determine most of the substances normally titrated with permanganate. The reagent was a weaker oxidant than the conventional reagent, however, and being insufficiently coloured to act as its own indicator, it was used in conjunction with barium diphenylamine sulphonate. Titrations were also effected potentiometrically, but it must be concluded that none of the trivalent manganese reagents is of practical value, for, although the pyrophosphate complexed reagent was used for the titration of iron in even 5 N hydrochloric acid, other reagents such as dichromate and ceric sulphate may be used similarly, and they possess a greater stability and wider range of application.

Potassium Ferrate

The possibility of using potassium ferrate as an oxidimetric reagent has been suggested by recent papers on the oxidation of arsenites[8]. Chromite has also been successfully determined[9]. A feature which militates against the use of the reagent is the necessity to use it in a strongly alkaline medium.

THE CLASSICAL REDUCTANTS

There has recently been a resurgence of interest in the classical reductimetric reagents, stannous, titanous and chromous chlorides.

Chromous Chloride

Flatt and Sommer[10], have made a detailed examination of the use of chromous salts as reductants, developing methods for the determination of tungsten and uranium in solutions warmed to 80° C., and for iron, copper, titanium, vanadium, chromium, molybdenum and tungsten in admixture[11]. Continental workers[12] have established that chromous chloride reduces hexavalent tungsten to the pentavalent state quantitatively in cold, concentrated hydrochloric acid. A method was

outlined for the determination of tungsten, in concentrates and ferro-tungsten, at ordinary temperatures with chromous chloride. More recently, American workers[13] have described a potentiometric titration of selenate and tellurate with chromous chloride in solutions containing high concentrations of sulphuric and hydrochloric acids at a temperature of 60°–70° C. Lingane and Pesock[14] pointed out that chromous chloride was the most powerful reductant used in titrimetric analysis, and have shown how a solution of accurately known equivalence may be prepared from standard dichromate by reduction with zinc amalgam in dilute sulphuric acid. A detailed study was also made of the potentiometric titration of Ti^{IV} and Fe^{III} ions[15], as a result of which it was concluded that iron was best determined in 1·8 N sulphuric acid, using a platinum indicator electrode against a saturated calomel electrode. Titanium was best titrated in 4 N sulphuric acid using a mercury indicator electrode. Iron and titanium together were determined by titration with the reagent in a medium 4 N with respect to sulphuric acid, using first of all a platinum indicator electrode for the iron, and switching over to the mercury electrode for the titanium titration.

Titanous Sulphate

Flaschka[16] has evolved a neat method for the stabilisation of titanous sulphate solutions, which makes the use of an inert atmosphere superfluous. The modification simply consists in filling the lower part of the burette with granulated cadmium or silver powder. An unusual preparation of the titanous sulphate solution is recorded in the paper. The calculated amount of titanium dioxide was fused with potassium bisulphate, and the mass dissolved in dilute sulphuric acid, and made up to the desired volume.

Stannous Chloride

One of the drawbacks to the use of stannous chloride as a titrant is the lack of an efficient visual indicator to mark the end-point of titrations. Kutschment and Gengrinovitsch[17] have recently proposed the use of cacotheline, and Szabo and Sugar[18] have used a double indicator technique employing ammonium thiocyanate and ammonium phospho-molybdate. In the former case, the cacotheline is not attacked by the stannous ions till all the iron (in a titration of ferric iron) is reduced ; a violet colour marks the end-point. In the latter method, the reduction of most of the ferric iron is marked by a fading of the ferric thiocyanate colour to straw yellow, whereupon ammonium molybdate and sodium phosphate are added. The phospho-molybdate is reduced to molybdenum blue at the end-point of the titration. Aluminium, manganese, zinc, lead, tungsten and arsenic do not interfere in the determination of iron in ores. In this respect, however, the reagent is in no way superior to mercurous nitrate, which in addition possesses stability, greater freedom from interference, and a better end-point. More recently, the same authors have made an extensive survey of the uses of stannous chloride, and have coined the term "Stannometry" to describe titrations employing stannous chloride. The titration of ferric iron was considered from a theoretical aspect and optimum conditions of acidity, temperature and time of heating were established for various determinations, as well as for interference from foreign ions. Chromium in the form of dichromate was determined by titration in 3 N hydrochloric acid with diphenylamine as indicator, while vanadium was determined in 3·7 N hydrochloric acid with the same indicator at room temperature. In the latter case, calcium carbonate was added to ensure a vigorous evolution of carbon dioxide during the titration. Ferricyanide was determined in a 7% hydrochloric acid medium in an atmosphere of carbon dioxide at room temperature. The formation of a clear blue colour in the titration medium marked the end-point of the titration. The authors suggest that this colour may be due to the formation of potassium ferrous ferrocyanide. Stannometric determinations of iodine, iodate and bromate were also described.

Application of the Complexones in Titrimetry

The term complexone, defined originally by Schwarzenbach, applies to a group of reagents including ethylenediaminetetraacetic acid (E.D.T.A.) nitrilotriacetic acid, and uramildiacetic acid, but it is mainly with the first reagent that most success has been achieved. These complexones owe their analytical powers to their remarkable metal binding properties. Pribil[20] has summarised the use of E.D.T.A. in titrimetry into three categories. In the first, a divalent metal ion reacts with the disodium salt of E.D.T.A. and the liberated hydrogen ions are titrated with standard alkali.

$$Me^{++} + H_2Y'' \longrightarrow MeY'' + 2H^+$$

In the second category, a weakly acidified solution of cation is titrated with a standard solution of a normal alkali salt of E.D.T.A. During titration the hydrogen ion concentration remains practically constant, but at the end-point a small excess of the reagent reacts with the hydrogen ions causing a sharp change in *p*H

$$Me^{++} + Y'''' \longrightarrow MeY''$$
$$Y'''' + 2H^+ \longrightarrow H_2Y''$$

In the final category, a direct titration with E.D.T.A. is again employed, but in this case a specific indicator for the cationic species being determined is present, and changes colour at the end-point when the cation has been completely complexed. Thus, for example, ferric iron may be titrated with E.D.T.A. using ammonium thiocyanate as indicator. By these methods it is possible to titrate a wide variety of cations including Li, Mg, Ca, Sr, Ba, Zn, Hg, Cd, Cu, Fe, Co, Ni, Ce and Mn. The reagent is most used for the determination of water hardness by direct titration of the dissolved calcium and magnesium salts. Indeed, it is the only really satisfactory method that has been devised for the direct titration of calcium.

Cobalt.

Lately Pribil and his research school, in a series of some fifteen papers, and Flaschka, working independently, have shown how useful the reagent can be in metallurgical analysis. Pribil and Malicky[21] have developed a method for the titration of cobalt, based on the method of Tomicek and Freiberger[22]. In the latter work, use was made of the fact that in ammoniacal solution both cobalti and cobalto-complexes of ammonia are formed, thus lowering the redox potential of the system to a value where it was possible to titrate divalent cobalt oxidimetrically with ferricyanide. In the complexone method, the complexonate of trivalent cobalt in acid solution was found to be more stable than the corresponding divalent cobalt compound, and the determination was effected by titration with ceric

sulphate to a potentiometric end-point at ordinary temperatures. Pribil's method has several unpleasant features, e.g., critical dependence on acidity, volume and the excess of complexone. It possesses an advantage over the Tomicek method, in that it is carried out in an acid solution, and thus may be used even in the presence of iron, aluminium, chromium and titanium, etc. Manganese is co-oxidised, and nickel interferes for reasons unknown.

Manganese.

A reductimetric and an oxidimetric method for the determination of manganese have been proposed by Pribil and co-workers. The oxidimetric method is suited to the determination of manganese in the presence of cobalt, and is based[23] on the fact that while both the complexonates of divalent manganese and divalent cobalt are oxidised by potassium dichromate, the tervalent cobalt compound is much more stable, and the manganese^{III} compound decomposes to the manganocomplexonate in hot solution. The excess dichromate is simultaneously reduced, so that the manganese may be determined oxidimetrically in an alkaline cyanide medium by standard potassium ferrocyanide. Copper and vanadium interfere critically, and must be removed.

In the reductimetric method[24], the manganese was oxidised by lead dioxide in the presence of complexone at room temperature, and titrated with ferrous sulphate within five minutes to a potentiometric end-point ; the determination was also finished iodometrically. The titration was best carried out in acetic acid, since mineral acids caused interference. It was necessary to remove tungsten and molybdenum before titration. Cobalt behaved in a manner similar to manganese but Cu, Pb, Zn, Ni, Al and Cr did not interfere.

Pribil and Svestka[25] outlined a similar method for cobalt in which the latter was oxidised, in the presence of E.D.T.A., by ceric sulphate at a temperature of 60° C. At the elevated temperature employed, the excess oxidant was reduced by the complexone, and the cobalt could therefore be titrated potentiometrically with chromous chloride. In the presence of manganese, dichromate was used as oxidant because ceric sulphate did not function satisfactorily. The mangani-complexonate decomposed at the elevated temperature, and did not interfere with the titration of cobalt.

Flaschka[26] has recently modified the Schwarzenbach methods for the determination, by direct titration with E.D.T.A., of the ions Mg, Ca, Zn, Cd, Mn, Cu, Fe, Ni, Hg and Pb, and carried out these titrations on the micro scale. The same author has also described a method for the complexonimetric determination of sodium[27], lead[28] and phosphate[29].

Lead—Sodium—Phosphate

Lead was titrated in a medium containing tartrate ions, buffered at *p*H 8–10, using Eriochrome Black T as indicator. In the presence of excess lead, a violet colour persisted until the end-point was reached, when it changed to "cornflower blue." Lead was titrated in the presence of zinc, nickel, copper, etc. when those ions were masked by addition of cyanide. Sodium was determined by titration of zinc after precipitation of sodium zinc uranyl acetate and solution of the precipitate in ammonium carbonate and ammonia ; the same indicator was used. Phosphate was precipitated as magnesium ammonium phosphate, and the magnesium determined in the usual way with E.D.T.A. Interference by calcium and other cations was prevented by adding complexone during precipitation.

The theoretical aspects of chelate complex formation as a basis for titration processes have been discussed by the pioneer of complexones, Schwarzenbach, in a recent paper[30]. Metal cations are considered as Lewis acids and their reaction with ligands during complex formation is compared to the addition of protons to a base. Complex formation with ligands such as cyanide and ammonia are generally unsatisfactory as a basis for titration procedures, because of the poor quality of the end-point. Schwarzenbach has shown, however, that complex formation takes on the nature of a neutralisation reaction when simple ligands are replaced by a polydentate group which is able to satisfy all the co-ordination requirements of the particular cation.

MISCELLANEOUS PROCEDURES

In these concluding paragraphs brief reference is made to some of the more interesting methods which have appeared in titrimetric analysis during the past three or four years.

Boron and Germanium

There have been several variations of the mannitol method for boron reported recently. Determinations of boron in ferroboron[31], magnesite[32], plating baths[33], metals and alloys[34] and steels[35,36] have been described. Blumenthal[35] separated boron from metal borides in steel by precipitation of the metals with barium carbonate and sodium hydroxide, bringing the borides into solution by means of a sodium carbonate fusion. The boron was then determined potentiometrically by titration after mannitol addition. On the other hand, Kelly[36] separated boron from the other metals present in steel by volatilisation as methyl boride, followed by titration with alkali using 0·04% bromothymol blue.

Cluley[37] has made use of the similar reaction of germanium with mannitol to evolve an alkalimetric method for germanium. The latter was initially separated from interfering elements by precipitation as sulphide. Arsenic was co-precipitated with germanium, but since only pentavalent arsenic interfered with the titration, this difficulty was obviated by reduction with sulphur dioxide. Traces of antimony and tin did not interfere, but larger amounts caused trouble by deposition of hydroxides or basic salts. A fixed *p*H titration method was used.

Silicon

Since the evolution of the well-known Kordon[38] method for the rapid determination of silicon in iron and steel, several minor variations have appeared, but recently a new method has been advanced by Wilson and Redman[39]. The method involves precipitation of the silicon as quinoline silico-molybdate. The precipitate was dissolved in standard sodium hydroxide, and the latter was then back-titrated with acid. A conductometric titration with lead nitrate has also been proposed by a continental worker[40], while yet another method[41] has been devised in which the silicon is precipitated as hexamethylenetetramine silico-molybdate. Dissolved in a slightly acid solution, the precipitate hydrolyses to ammonia and formaldehyde, which is treated with a standard bisulphite solution, and back-titrated with standard iodine.

Selenium and Tellurium

A rapid titrimetric method for the determination of selenium in the presence of tellurium, using pyrophosphate as the masking agent and iodine monochloride as catalyst, has been developed by Russian workers[42]. Another control method for metallic copper and pyritic materials involves distillation of selenium tetrabromide. Cobalticyanide and potassium iodide are added, and the determination finished by titration with standard thiosulphate[43]. Other recent methods have used potentiometric titration with chromous chloride in 9 N hydrochloric acid at 65° C.[44], and precipitation with standard silver nitrate at *p*H 7, with back titration of the excess silver by means of potassium chloride[45].

Ruthenium has been recommended as a catalyst for the manganometric determination of tellurium[46]. More recently Noakes[47] described a method for tellurium in copper, in which the former was separated with hypophosphite, dissolved with bromine and titrated with iodine after addition of potassium cobalticyanide and sodium hypophosphite. Others[48] have shown that while only reagents such as chromous and titanous salts, which are unstable in air, are powerful enough to carry out a reductimetric titration of tellurous acid, the reaction of quadrivalent tellurium with thiosulphate is induced by the addition of iodide to form the iodotellurite ion. Direct titrations were carried out, but a back titration with iodine was preferred.

Zinc

The zinc/ferrocyanide titration is a well-established procedure for the determination of zinc. Several internal indicators are available for the titration, and hitherto the best of these was probably *o*-dianisidine, which changes from brick-red to pale blue-green. Belcher and Nutten[49], investigating the applications of substituted benzidines and related compound in analytical chemistry, have proposed the use of naphthidine for this determination. The colour change at the end-point is from pink-red to white. Milner[50] has applied the new indicator to the determination of zinc in non-ferrous alloys and rubber ash. In Milner's method for aluminium alloys, aluminium bronzes and white metals, the zinc was separated by precipitation with hydrogen sulphide. In tin bronzes, oxine was used for separation. Later, Belcher, Nutten and Stephen[51] proposed the use of 3,3′ dimethylnaphthidine as indicator. The substituted naphthidine was a ten times more sensitive indicator, and the end-point colour was more stable. The sulphonic acid derivatives of both naphthidine and dimethylnaphthidine were subsequently prepared and compared with the free bases and each other[52]. The colours given by the sulphonic acids were superior to those given by the free bases, but were considerably less stable. The application of diphenylthiocarbazone (dithizone) to the zinc/ferrocyanide titration has recently been investigated by Mehlig and Guill[53]. The indicator was concentrated in a layer of carbon tetrachloride but, due to the *p*H requirements of the titration under these conditions, the method would appear to be less satisfactory than the napthidine and dimethylnaphthidine methods. A similar method using diphenylcarbazone was described by Evans[54].

The iodometric determination of zinc was the subject of an investigation by Maun and Swift[55]. Under the conditions of the procedure finally recommended by the authors, the necessity for stepwise addition of ferricyanide and successive titrations of iodine was eliminated and a stable end-point obtained. An empirical factor of 1·019 was used to calculate the amount of zinc.

Caley, Gordon and Simmons[56] have made use of the insolubility of zinc oxalate, using ethyl oxalate as precipitant, to devise a method in which the precipitate was subsequently dissolved in acid, and titrated with standard premanganate. Tillu[57] has evolved the most recent method for the titration of zinc, however, in a process in which zinc was precipitated as its basic carbonate by the addition of sodium bicarbonate to the solution containing zinc. The basic carbonate was dissolved in sodium thiosulphate to liberate an equivalent amount of alkali, and the latter was titrated with 0·1 N hydrochloric acid. Cadmium reacted similarly and could be determined in the same way, by precipitation as hydroxide. Tillu recommended the method for zinc in alloys, but no analysis figures other than those for pure zinc and cadmium solutions were given.

Aluminium—Titanium—Cobalt

A method for the determination of aluminium in brass and all types of copper-base alloys, dependent on selective precipitation of the aluminium as its benzoate complex, has been outlined by Milner and Townend[58]. Copper and iron were reduced with hydroxylamine hydrochloride, and the benzoate complex precipitated with ammonium benzoate at *p*H 4. The aluminium was re-precipitated by oxine, the precipitate dissolved in acid, and titrated in the usual way with potassium bromate.

Beck and Szabo[59] have re-investigated the acidimetric titration of aluminium. In their method, an aliquot of aluminate solution was titrated with standard hydrochloric acid till precipitation of the hydroxide was complete, and another aliquot was treated with alkali fluoride, and titrated to the same *p*H. The difference in the two titres was multiplied by a factor of 0·899 to give the amount of aluminium.

Shippy[60] has carried out a rapid titration of titanium with permanganate, using methylene blue as indicator, while Vecchi[61] has modified the usual silicate analysis method by titrating the titanium with sodium dichromate. More interesting, however, are two recent methods in which titanium^{III} has been oxidised with vanadium pentoxide during solution, the excess pentoxide being determined with ferrous iron[62], and in which acetic acid and ammonium sulphate were used to complex titanium^{III} so that it could be titrated directly with ceric sulphate, without oxygen interfering[42]. Cacotheline was used as indicator in the latter method, and the presence of iron did not interfere with the determination. Bischoff[63,64] determined titanium by titration with ferric iron after reduction with metallic iron.

Laitinen and Burdett[65] determined cobalt iodometrically, by fusion of the cobalt sample with pyrosulphate and oxidation with peroxide in the presence of potassium bicarbonate. The tervalent cobalt was then reduced with iodide, and the liberated iodine titrated. The interference of small amounts of iron and nickel was overcome by the masking action of fluoride ions. Tomicek[66] and co-workers have used ferricyanide in strongly alkaline solutions, and others have precipitated as arsenate and titrated bromometrically[67].

Copper

Several methods have been advanced for the titrimetric determination of copper during the past few years. These include an extractive titration with dithizone[68] and determinations of the cuprous ion by titration with permanganate, dichromate and ceric sulphate[69]. Burriel and Lucena Conde[70] have evolved a titrimetric finish to the thiocyanate method, whereby the cuprous thiocyanate is dissolved in ferric alum and the ferrous sulphate thus formed is titrated oxidimetrically. A similar method in which cuprous cyanide is precipitated and treated similarly with ferric iron and subsequently dichromate was investigated by the same authors[71]. The titration of copper in steels with diphenylthiocarbazone has been described by Russian workers[72]. Several variations of the iodometric determination of copper have been examined. For example, sodium bromide has been used to convert cupric copper to the complex bromide ion and the latter titrated with thiosulphate[73]. Brasted[74] has suggested an iodometric method whereby copper and iron may be determined together on two aliquots of the same solution. Preneutralisation, boiling, evaporation and buffering in a nitric acid medium was eliminated by treating the nitric acid with sulphamic acid, thus removing the troublesome nitrous acid. The iron and copper were determined together by the iodometric method on one aliquot, and the copper was determined successfully in the second aliquot after masking the ferric ion with fluoride and buffering with phthalate or acetate ions.

A critical survey of the iodometric method for copper has been made by Meites[75]. The conventional iodometric method requires the addition of just sufficient potassium iodide to precipitate the cuprous iodide, and keep the liberated iodine in solution. The titration of this solution with standard thiosulphate leads to low results because of absorption of iodine on the surface of the cuprous iodide. Foote and Vance[76] showed that addition of thiocyanate near the end-point prevented this absorption by the formation of the more insoluble cuprous thiocyanate on the surface of the precipitate, thus minimising the absorption of iodine. Hammock and Swift[77] used the thiocyanate modification of Foote and Vance to analyse several copper alloys and obtained excellent results. They confirmed the original observations of Foote and Vance, and investigated the use of other protective agents, such as shellac. Scott's[78] method involves the addition of sufficient iodide to keep the cuprous iodide in solution, thus eliminating errors usually associated with the separation of a solid phase during titration. Meites recommended this little known method of Scott as being superior to the modification of Foote and Vance. The interfering effect of various ions was investigated; iron was complexed as ferri-fluoride, and arsenic did not interfere in the *p*H range 4·7–6·3, but bismuth in amounts exceeding 10 mg./100 ml. of solution interfered by masking the end-point. Antimony did not interfere above *p*H 4·8, and lead, silver and mercury caused no difficulty unless present in large amounts. High concentrations of chromium, cobalt and nickel interfered in the obvious way by masking the end-point colour change. Molybdenum, uranium and vanadium could only be tolerated in trace amounts. None of the common anions interfered with the determination.

Other methods which have been reported recently include a bromometric tiration of hydrazine following the precipitation of copper with hydrazine sulphate using tropeolin 00, fuschin or thymol blue as indicators[79] and a new departure involving precipitation of the ammonium pyridine thiocyanate compound of cupric copper and titration of the excess thiocyanate with silver nitrate[80]. The titrimetric method with mercurous nitrate has already been discussed, and seems to offer a speedy and accurate means of carrying out the determination.

Nomenclature in Titrimetry

In conclusion, the recent report of the committee on nomenclature in the division of analytical chemistry of the American Chemical Society is noteworthy.[81] Acidimetry and alkalimetry are defined respectively as measurement of the concentration of an alkali by titration with a standard solution of an acid, and measurement of the concentration of an acid by titration with a standard solution of an alkali. This is the nomenclature generally accepted in this country, but the definition of iodometry as measurement of the concentration of a substance by titration with standard iodine is generally referred to in Britain, and on the continent, as iodimetry, whilst the titration of iodine by a substance such as thiosulphate, which we generally refer to as iodometry, becomes "thiosulphatimetry" in American nomenclature. It is doubtful, in the present author's opinion, whether analytical chemists in this country, or indeed in America, will refer to "the thiosulphatimetric determination of copper" in future years, but, nevertheless, the recommendation of these definitions by a committee of such renowned chemists is a valuable contribution at the present time, when new terms and doubtful definitions abound. The report carefully stresses points that should be known to all analytical chemists, such as the fact that "volumetric" and "titrimetric" are not synonymous, and that the commonly found expression "titrimetric determination" is superfluous, since the term titration denotes determination.

REFERENCES.

1 Tourky, A. R., Farah, M. Y., and El. Shamy, H. K. *Analyst*, 1948, **73**, 258, 262, 266.
2 Belcher, R., and West, T. S. *Anal. Chim. Acta*, 1951, **5**, 260, 268, 360, 364, 472, 474, 546. Ibid., 1952, **7**, 740
3 Bradbury, F. R., and Edwards, E. G. *J. Soc. Chem. Ind.*, 1940, **59**, 96 T.
4 Pribil, R., and Uzel, R. *Coll. Czech. Chem. Comm.*, 1938, **10**, 330.
5 Beck, G. *Mikrochim. Acta*, 1937, **2**, 289.
6 Ubbelohde, A. R. J. P. *J. Chem. Soc.*, 1935, 1,605.
7 Belcher, R., and West, T. S. *Anal. Chim. Acta*, 1951, **6**, 322.
8 Shreyer, J. M., Thompson, G. W., and Ockerman, L. T. *Anal. Chem.*, 1950, **22**, 691.
9 Idem. *Ibid.*, 1950, **22**, 1,426.
10 Flatt, R., and Sommer, F. *Helv. Chim. Acta*, 1942, **25**, 684.
11 Idem. *Ibid.*, 1944, **27**, 1,518, 1,522.
12 Tschernikov, J. A., and Gorjuschina, V. G. *Zav. Lab.*, 1945, **11**, 137.
13 Lingane, J. J., and Niedrach, L. *J. Amer. Chem. Soc.*, 1948, **70**, 1,997.
14 Lingane, J. J., and Pesock, R. L. *Anal. Chem.*, 1948, **20**, 425.
15 Lingane, J. J. *Ibid.*, 1948, **20**, 797.
16 Flaschka, H. *Anal. Chim. Acta*, 1950, **4**, 242.
17 Kutschment, M. L., and Gengrinovitsch. *Zav. Lab.*, 1945, **11**, 267.
18 Zabo, Z., and Sugar, E. *Anal. Chem.*, 1950, **22**, 361.
19 Idem. *Anal. Chim. Acta*, 1952, **6**, 293.
20 Pribil, R. *Coll. Czech. Chem. Comm.*, 1949, **14**, 320.
21 Pribil, R., and Malicky, V. *Ibid.*, 1949, **14**, 413.
22 Tomicek, O., and Freiberger, F. *J. Amer. Chem. Soc.*, 1925, **47**, 801.
23 Pribil, R., and Simon, V. *Coll. Czech. Chem. Comm.*, 1949, **14**, 454.
24 Pribil, R., and Horacek, J. *Ibid.*, 1949, **14**, 626.
25 Pribil, R., and Svestka, L. *Ibid.*, 1950, **15**, 31.
26 Flaschka, H. *Mikrochemie*, 1952, **39**, 38.
27 Idem. *Ibid.*, 1952, **39**, 391.
28 Idem. *Ibid.*, 1952, **39**, 315.
29 Flaschka, H., and Holasek, A. *Ibid.*, 1952, **39**, 101.
30 Schwarzenbach, G. *Anal. Chim. Acta*, 1952, **7**, 141.
31 Sabinina, L. E., and Styunkel, T. V. *Zav. Lab.*, 1947, **13**, 752.
32 Hazel, W. M., and Ogilvie, G. H. *Anal. Chem.*, 1950, **22**, 697.
33 Wogrinz, A., and Kudernatsch, G. *Prakt. Chem.*, 1950, 197.
34 Bertiaux, L. *Chim. Anal.*, 1948, **30**, 252.
35 Blumenthal, H. *Anal. Chem.*, 1951, **23**, 992.
36 Kelly, M. W. *Ibid.*, 1951, **23**, 1,335.
37 Cluley, H. J. *Analyst*, 1951, **76**, 517.
38 Kordon, F. *Archiv fur das Eisenhuttenwesen*, 1945, **18**, 139.
39 Wilson, H. N., and Redman, H. N. *Analyst*, 1949, **74**, 243.
40 Berkovich, M. T. *Zav. Lab.*, 1950, **16**, 538.
41 Duval, C. *Anal. Chim. Acta*, 1947, **1**, 33.
42 Syrokomskii, V. S., and Silaeva, E. V. *Zav. Lab.*, 1949, **15**, 1,015.

43 McNutty, J. S., Center, E. J., and McIntosh, R. M. *Anal. Chem.*, 1951, **23**, 123.
44 Lingane, J. J., and Mates, I. *J. Amer. Chem. Soc.*, 1947, **69**, 277.
45 Ripan, R., and Popa, G. *Rev. Stiintifica, V. Adamachii*, 1946, **32**, 45.
46 Lang, R. *Z. Anal. Chem.*, 1948, **128**, 484.
47 Noakes, F. D. L. *Analyst*, 1951, **76**, 542.
48 Johnson R. A., and Fredrickson, D. R. *Anal. Chem.*, 1952, **24**, 866.
49 Belcher, R., and Nutten, A. J. *J. Chem. Soc.*, 1951, 547.
50 Milner, G. W. C. *Anal. Chim. Acta*, 1952, **6**, 226.
51 Belcher, R., Nutten, A. J., and Stephen, W. I. *J. Chem. Soc.*, 1951, 1,520.
52 Idem. *Ibid.*, 1952, 1,269.
53 Mehlig, J. P., and Guill, A. P. *Anal. Chem.*, 1951, **23**, 1,876.
54 Evans, B. S. *Analyst*, 1946, **71**, 455, 460.
55 Maun, E. K. , and Swift, E. H. *Anal. Chem.*, 1949, **21**, 1,876.
56 Caley, E. R., Gordon, L., and Simmons, G. A. *Ibid.*, 1950, **22**, 1,060.
57 Tillu, M. M. *Ibid.*, 1952, **24**, 1,495.
58 Milner, G. W. C., and Townend, J. *Analyst*, 1951, **76**, 424.
59 Beck, M., and Szabo, G. *Anal. Chim. Acta*, 1952, **6**, 316.
60 Shippy, B. A. *Anal. Chem.*, 1949, **21**, 699.
61 Vecchi, G. *Bull. Ecole. Poly. Tech., Jassy*, 1948, **14**, 751.
62 MacCardle, L. E., and Scheffer, E. R. *Anal. Chem.*, 1951, **23**, 1,169.
63 Bischoff, F. *Mikrochemie*, 1951, **36/37**, 251.
64 Idem. *Z. Anal. Chem.*, 1950, **130**, 195.
65 Laitinen, H. A., and Burdett, L. W. *Anal. Chem.*, 1951, **23**, 1,268.
66 Tomicek, O., Sandl, Z., and Simon, V. *Coll. Czech. Chem. Comm.*, 1949, **14**, 20.
67 Portnov, A. I. *Zhur. Obshch. Khim.*, 1948, **18**, 601.
68 Schonk, C. H. *Chem. Weekblad.*, 1946, **42**, 295.
69 Hatch, L. F., and Estes, R. R. *Ind. Eng. Chem. Anal.*, 1946, **18**, 136.
70 Burriel, F., and Lucena Conde, F. *Anal. Real. Soc. Espan. Fis. y Quim.*, 1948, **44**, 95.
71 Idem. *Anal. Chim. Acta*, 1948, **2**, 230.
72 Supranovich, I. B., and Konovalova, A. B. *Zav. Lab.*, 1948, **14**, 1,061.
73 Ehler, K. *Z. Anal. Chem.*, 1949, **129**, 93.
74 Brasted, R. C. *Anal. Chem.*, 1952, **24**, 1,040.
75 Meites, L. *Ibid.*, 1952, **24**, 1,618.
76 Foote, H. A., and Vance, J. E. *Ibid.*, 1936, **8**, 119.
77 Hammock, E. W., and Swift, E. H. *Ibid.*, 1949, **21**, 975.
78 Scott. Standard Methods of Analysis, Van Nostrand Co., N.Y. 1939, 5th Edn., 368.
79 Raikhinshtein, T. G. *Zav. Lab.*, 1949, **15**, 1,407.
80 Orth, B. *Mitt. Chem. Forsch. Inst. Ind. Osterr.*, 1949, **3**, 94.
81 Committee on Nomenclature, Div. of Anal. Chem., *Amer. Chem. Soc.*, June, 1952, *Anal. Chem.*, 1952, **24**, 1,348.

Miscellaneous Microchemical Devices

XXVII.—A Simple Low-Pressure Hydrogen Sulphide Generator

By J. T. Stock and P. Heath

(*Norwood Technical College, London, S.E.*27)

IN qualitative inorganic analysis, treatment with hydrogen sulphide may be effected either by bubbling the gas through the solution or by shaking the latter in an atmosphere of the gas. Because the surface-to-volume ratio is greater than in the macro method, the "shaking" technique is really useful on the semi-micro scale. Further, the need for high-pressure generators is eliminated, an ordinary Kipp generator being quite satisfactory[1].

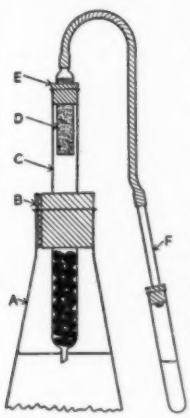


Fig. 1—Simple Micro Hydrogen Sulphide Generator.

Even simpler is the generator shown in Fig. 1. The 500-ml. conical flask *A* is about two-thirds filled with diluted (1 : 1) hydrochloric acid. Cork *B* is grooved to allow free entry of air and has a large central hole in which container *C* is a smooth sliding fit. The charge in *C* is broken iron sulphide stick. A length of glass tubing drawn down at the upper end and lightly packed with glass wool forms gas scrubber *D*. Jointing *E* is merely a short length of soft rubber tubing.

The solution is treated with hydrogen sulphide in a 75 mm. × 10 mm. micro test tube. Connection between test tube and generator is by delivery attachment *F*. This is a piece of 5 mm. outside diameter glass tubing closed to about 1 mm. bore at the lower end and carrying a short length of rubber tubing fitting snugly into the mouth of the test tube[1].

Operation is as follows :—

(i) Insert the delivery attachment into the test tube and connect to the generator as shown.

(ii) Slide container *C* downwards until most of the charge is below the acid-level. The bottom of the gas scrubber must however, remain well above this level.

(iii) Gently ease the test tube from the delivery attachment and, holding the latter almost touching the mouth of the test tube, allow about 10 seconds to displace the air from the apparatus.

(iv) Re-attach the test tube and agitate its contents for about a minute. This is easily done by lightly holding the upper part of the test tube and tapping or flicking near the bottom with the other hand.

(v) Having returned container *C* to its original position (important !), remove the test tube and delivery attachment.

The non-observance of (v) is very obvious—much more so than the incomplete closure of the stopcock or spring-clip needed to control the output from a generator of conventional type.

Recharging is very easy and may be further facilitated by keeping a small stock of charged iron sulphide containers complete with scrubbers. When required, these are exchanged for spent ones, the latter being cleaned and recharged at leisure.

1 Stock, J. T., and Heath, P., *Metallurgia*, 1950, **42**, 44.

Proposed Weights and Measures Legislation

The President of the Board of Trade recently announced in the House of Commons that he was arranging consultations about the recommendations of the Committee on Weights and Measures Legislation with the trading, local authority and other interests concerned. He said that on account of the wide variety of the recommendations and the extensive nature of the consultations, legislation would not be introduced for some time.

Consultations are now beginning and the Board would be glad to receive comments on any of the Committee's recommendations from interested parties. It would be of great assistance if persons or organisations intending to submit comments would give the Board notice of their intention to do so as soon as possible, indicating the recommendations on which they propose to comment. All correspondence should be addressed to the Controller, Standards Department, Board of Trade, 26, Chapter Street, London, S.W.1.

British Standard Analytical Methods for Iron and Steel

METHODS FOR THE ANALYSIS OF IRON AND STEEL PART 27—DETERMINATION OF VANADIUM IN CARBON AND LOW ALLOY STEELS. (B.S.1121 Part 27 : 1952). PRICE 2s.

PART 28—DETERMINATION OF GRAPHITIC AND COMBINED CARBON IN PIG AND CAST IRON. (B.S.1121 Part 28 : 1952). PRICE 2s.

THE British Standards Institution has recently published the above additional parts of B.S.1121.

Part 27 is for determining up to 1% of vanadium, and except at very low vanadium contents the alloying elements normally present in low alloy steel do not interfere. The principle of the method is solution of the sample in phosphoric-sulphuric acid, oxidation of the iron with nitric acid followed by oxidation of the vanadium at atmospheric temperature by means of potassium permanganate. The excess reagent is destroyed by the addition of sodium nitrite and the oxidised vanadium is reduced with an excess of ferrous ammonium sulphate. This is back titrated with standard potassium dichromate using barium diphenylamine sulphonate indicator.

Part 28 deals with the determination of graphitic carbon in irons containing up to 4½% carbon. Determinations of total and graphitic carbon are carried out separately and the combined carbon is calculated by difference. The total carbon is determined by combustion using a procedure similar to that described in B.S.1121, Part 11 "Determination of Carbon in Steel and Low Carbon Ferro-Chromium." The graphit carbon is determined by decomposing the sample wi nitric acid, filtering off the residual graphite, igniting t residue in a stream of oxygen and absorbing and wei ing the carbon dioxide as described in B.S.1121, Part 1

Copies of these standards may be obtained from t British Standards Institution, Sales Branch, 24, Victor Street, London, S.W.1.

The Royal Society

Election of Officers

THE following have been elected Officers and Council the Royal Society for the ensuing year :—

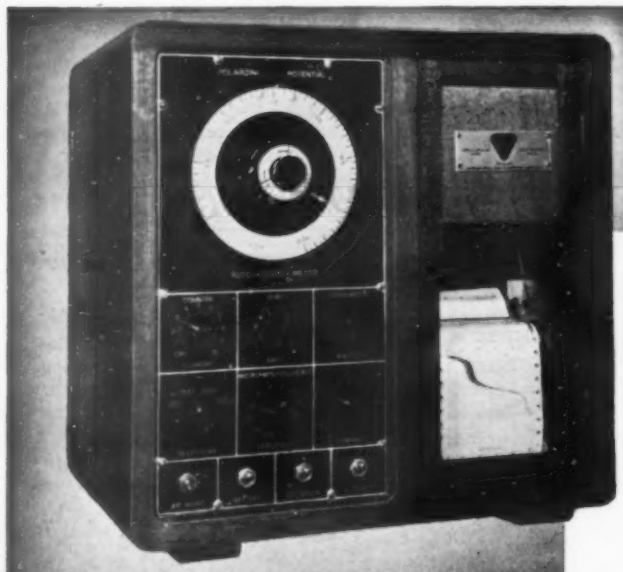
President : Dr. E. D. Adrian, O.M.

Treasurer and Vice-President : Sir Thomas Merto

Secretaries and Vice-Presidents : Sir Edward Sali bury, C.B.E., and Sir David Brunt.

Foreign Secretary : Sir Cyril Hinshelwood.

Members of Council : Professor P. A. Buxto C.M.G. ; Mr. H. Constant, C.B.E. ; Professor P. Dee, C.B.E., Professor E. C. Dodds, M.V.O. ; Profes H. J. Emeleus ; Sir Howard Florey (Vice-President Professor D. R. Hartree ; Professor E. G. T. Liddel Professor E. J. Maskell ; Professor R. A. McCanc Professor H. H. Plaskett ; Professor W. J. Pug O.B.E. ; Professor Alexander Robertson ; Dr. Stoneley ; Professor G. Temple, and Professor C. Yonge.



TINSLEY

Single unit — Ink recording

POLAROGRAPH

For rapid and accurate micro-chemical analysis.

★ Completely undamped waves *and* high precision damping.

★ 34 current ranges, multi-speed potentiometer and counter current.

★ Analysis of Metals, Inorganic and Organic substances.

★ Simultaneous estimations of several constituents on one Polarogram.

A comprehensive advisory service on methods is available without obligation.

Please write for leaflet A.7.

TI

TINSLEY (INDUSTRIAL INSTRUMENTS) LIMITED

NORTH CIRCULAR ROAD, LONDON, N.W.10. ELGar 6081